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THE FINE STRUCTURE OF MATTER

PART II

MOLECULAR POLARIZATION

A COMPREHENSIVE TREATISE ON ATOMIC AND MOLECULAR STRUCTURE

By C. H. DOUGLAS CLARK

VOLUME I.

THE ELECTRONIC STRUCTURE AND PROPERTIES OF MATTER

An Introductory Study of certain Properties of Matter in the Light of Atomic Numbers.

CONTENTS: Part I.—GENERAL INTRODUCTION. The Classification of the Elements—The Classification of Atomic Electrons—Line Spectra and Multiplicity—The Transitional and Rare Earth Elements—Valency and Chemical Combination. Part II.—PHYSICAL PROPERTIES AND MOLECULAR CONSTITUTION. Melting-Points and Boiling-Points—Atomic and Molecular Volumes—Atomic and Ionic Radii—Electrical Conductivity—Magnetic Susceptibility—Atomic Magnetic Moments—Cohesional and Other Properties.

VOLUME II. (IN THREE PARTS ISSUED SEPARATELY)

THE FINE STRUCTURE OF MATTER

The Bearing of Recent Work on Crystal Structure, Polarization and Line Spectra.

CONTENTS · Part I.—X-RAYS AND THE STRUCTURE OF MATTER. Space Lattices and X-Rays—The Crystal Structure of Elements—The Crystal Structure of Inorganic Compounds of Type AB—The Crystal Structure of Inorganic Compounds of Type AB_2—The Crystal Structure of Compounds of further Inorganic Types—The Crystal Structure of Compounds of Organic Types—The Crystal Structure of Colloids and Amorphous Substances—The Crystal Structure of Alloys, Intermetallic Compounds and Solid Solutions—Crystal Structure and Molecular Constitution. Part II.—MOLECULAR POLARIZATION Dielectric Constants—The Debye Theory of Polarization—Molecular Refraction—Polar Molecules—Molecular Fields. Part III.—THE QUANTUM THEORY AND LINE SPECTRA. The Quantum Theory—The General Principles of Line Spectra—The Multiple Structure of Lines—Line Spectra and the Periodic System.

VOLUME III. IN PREPARATION

THE INTERPRETATION OF BAND SPECTRA

An Account of Spectroscopic Investigation in the Field of Molecular Structure.

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THE FINE STRUCTURE OF MATTER

The Bearing of Recent Work on Crystal Structure, Polarization and Line Spectra

Being
VOLUME II
of
A COMPREHENSIVE TREATISE OF ATOMIC AND MOLECULAR STRUCTURE

PART II:

MOLECULAR POLARIZATION

BY
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To

MY MOTHER

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GENERAL PREFACE

THE progress of atomic and molecular theory in recent times has proved remarkably rapid and extensive. The subject has advanced along many different lines more or less independently and the research worker in a specialized branch often encounters no little difficulty in keeping in touch with developments not in his immediate sphere of thought. It has become increasingly difficult, though surely not less important, to correlate work carried out in different branches. It is in the hope that these diverse researches may be enabled to be considered more readily in inter-relation with each other and in respect of the effect of each contribution to the whole that the author has essayed the present task. A work which attempts to view the situation along various avenues of approach may perhaps also prove of value in enabling a given fact or principle to be found conveniently in the original literature.

The introduction of electron spin into physical theory by Uhlenbeck and Goudsmit in 1925 has greatly clarified the general theoretical situation, so that the present time seems appropriate for a review of the present summarizing kind. Moreover, it would appear that sufficient time has elapsed since this important contribution was made for its true significance to be appreciated.

The general plan of the work is that of separate volumes bearing individual titles, each volume being as far as possible complete in itself as an expression of some leading thought. The first three volumes at present projected are intended to deal with different aspects of more purely physical questions. Further volumes are in contemplation which shall be descriptive of matters of special chemical importance.

The treatment is non-mathematical, a few mathematical proofs being collected in appendices to certain chapters. The conclusions reached in *The Basis of Modern Atomic Theory*

(Methuen, 1926), designed to give the experimental background of the fundamental principles, are here assumed, thus saving a considerable amount of space Methods of reasoning from the results obtained, rather than details of experimental procedure and technique, form the main concern of the present work

References to the original literature necessarily occupy a considerable amount of space Titles of papers are given in full, it is hoped that this procedure will facilitate ease of reference Every attempt has been made to ensure that the references shall be not only as complete as possible, but also accurately quoted To save space, references to summarizing papers are frequently given, so that in these cases many of the papers quoted in them need not be repeated in the lists

The thanks of the author are warmly accorded to numerous colleagues who have helped him with advice and co-operation It is with a deep sense of gratitude that he extends his cordial appreciation of this assistance, which has proved of the greatest value On the other hand, the author accepts sole responsibility for design and execution, individual expression of opinion and any slips or defects overlooked during revision

Each volume is brought up to date to the time of publication as far as possible The author would be pleased to be informed of anything of significance which he may have inadvertently overlooked

If the work is found to encourage in any measure the wider study and investigation of problems arising in a fascinating field of modern thought, or to assist and direct the energies of the army of workers, the author will be amply repaid for time and care entailed in its production

C H D C.

Department of Inorganic Chemistry,
The University of Leeds
April, 1934

PREFACE TO VOLUME II

MODERN physics has trained her most powerful weapons on the closely guarded strongholds of Nature This is particularly true in the field of the fine structure of matter, where the scientific combatant, safely entrenched on high ground already won, glimpses with justifiable satisfaction the fertile lowlands where he may hope to reap the fruits of his campaign Prominent amongst experimental means which have proved themselves especially efficient are the X-ray, the dielectric cell, and the spectroscope La Mer,* in the introduction to a symposium on molecular constitution held under the auspices of the American Chemical Society in 1929, recognized these three instruments as assuming special significance at that time Progress in the intervening period has done much to establish their importance This matter forms the theme of the present volume, the three named experimental methods being treated in Parts I, II and III respectively (issued for convenience in three separate bindings)

Part I is devoted to discussion of crystal and related structures as determined by X-rays Space is economized by reference to the valuable *Strukturbericht* (1931) prepared by Ewald and Hermann in connection with the *Zeitschrift fur Kristallographie* The second volume of this work, covering the period 1928 to 1932, has appeared this year (1936), and was therefore not available to the author during the preparation of his manuscript The method of classification of crystal structures suggested in the 1931 volume has been followed as closely as possible, apart from certain amendments, especially in dealing with organic and intermetallic compounds (Tables XXIII, XXIV, XXV and XXVII) Complex inorganic compounds are classified according to number of atoms per molecule for

---

*V K La Mer *Chemical Reviews*, 1929, 6, 445–450 ease in reference It is hoped that no outstanding results in the period under review have been overlooked Space is saved in references by not repeating papers cited by Ewald and Hermann the present lists are intended to be used in conjunction with their work, so that it is hoped that the experimental data on any given substance may be found quickly and conveniently in the original literature In the final chapter on the relation between crystal structure and chemical constitution, the author gratefully acknowledges the assistance he received from the fruitful discussion held under the auspices of the Faraday Society in 1929

The Debye theory of polarization, Fajans' theory of deformation and the derivation and meaning of dipole moments form the leading themes of Part II The more refined measurements of dielectric constants and refractive indices have played an important part The comprehensive *Table of Dipole Moments* (1934) of Hampson and Marsden published in the *Transactions of the Faraday Society*, has proved itself remarkably useful in again saving reference space and increasing the availability of experimental data A detailed account of work on the Kerr Effect closes the Part Polarization phenomena are found to take their place alongside the other main avenues of approach in providing valuable information about the structure and stereochemistry of organic and inorganic compounds

Discussion of the results of spectroscopy is commenced in Part III, with special reference to newer adaptations of the quantum theory in relation to line spectra The treatment is continued in Vol 3 dealing with band spectra, but the part given separately here seems well able to stand alone, as an introduction to the study of spectra The derivation of the quantum numbers, omitted from Vol 1 5, is given as carefully as possible In this connection, acknowledgment is due to the monograph and list of references due to Gibbs in his *Line Spectra of the Elements* I *Early observations and Systems of Classification* (1931), published in the *Review of Modern Physics* The present author is satisfied if he has met with any success in his attempt to impart to those unfamiliar with recent developments the fascination that he feels in that romantic department of atomic science, the interpretation of spectra and the inward nature of the periodicity of the elements More purely chemical considerations receive some attention in the closing chapter of the volume An electronic periodic table has appeared in time to be included in the Appendix to Part III

Even with the saving of space effected by utilization of the summarizing works mentioned above and of others referred to in the text, it was soon realized that a very large number of references still remained The question of the amount of space which should be devoted to their accommodation occupied the attention of the author for some time, as a consequence of which it was decided to depart from previous practice to a certain extent, by omitting the titles of papers in those chapters which dealt mainly with experimental data It was found possible to retain the titles in other cases, where theoretical aspects seemed particularly important (chapters I, XI, XIV, XV, XVI and XVIII) It is hoped that the change of policy necessitated by exigencies of space will not diminish the usefulness of the book

The preparation of a work of the present kind by one individual must necessarily be spread over a considerable period of time, and it was deemed preferable to bring the whole volume up to a certain date rather than to add to portions (written at later times) work done after the date The book is designed to cover the period up to that surveyed by *Science Abstracts* (*Physics*) of January, 1935 From this definite date, more recent work may be found in later numbers of the above and other lists of abstracted papers

References in the text to *The Basis of Modern Atomic Theory*, mentioned in the General Preface, are given as *Basis*, with sectional reference number

The author desires to acknowledge with thanks the kind permission of the Editors of the *Philosophical Magazine* to reproduce Fig CXIII, and to the Editor of the *Proceedings of the Leeds Literary and Philosophical Society* in respect of Figs CVII and CXXII In all cases, the diagrams have been specially drawn for this work, and the author's thanks are due to Mr. R G A Dimmick, who prepared some of the original, drafts for this purpose The kind permission of Professor Planck and Messrs Methuen, Ltd , to reproduce the quotation facing page 1 is gratefully acknowledged The author's thanks are also accorded to Miss L Wilson, for assistance in indexing and proof-reading

C H D C

Department of Inorganic Chemistry,
The University of Leeds
November, 1936

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LIST OF SYMBOLS

(VOLUMES I, II, III)

Note—As far as possible, in specifying quantum numbers, capital letters refer to atoms, small letters to electrons, large Greek letters to molecules, small Greek letters to molecular electrons

Symbol	
A	Atomic weight, area, number of molecules in ground state, Mendeljéeff group, amplitude of wave motion, any constant quantity
B	Constant of rotational spectra, limiting area, Mendeljéeff group, magnetic induction, any constant quantity
C	Curie's constant, specific heat, at constant volume C_v, at constant pressure C_p, any constant quantity
D	Density, electric displacement, spectral series, heat of dissociation, constant of rotational spectra, diffusion constant
E	Energy, molecular surface energy, electric field, number of outermost electrons, extension coefficient, electron affinity
F	Force, electric force acting on a molecule, free energy; spectral series, lowering of surface tension, wave-number of molecular spectral term
G	Co-ordination number
H	Magnetic field strength, quantity of heat, Hermitian polynomial
I	Moment of inertia, ionization energy, electric moment of unit volume (polarization), intensity of magnetization, integration constant.
J	Inner quantum number, potential energy; ionization potential, interaction integral
K	Rotational quantum number, Kerr constant; symbol for absolute temperature, equilibrium constant; any constant quantity.
L	Serial quantum number, heat of solution.

Symbol	
M	Magnetic quantum number; constant of rotational fine structure of electronic bands; molecular weight.
N	Avogadro number; frequency of revolution; periodic group number; Weiss molecular field constant.
O	Optical representation of energy level.
P	Vapour pressure; parachor; pressure of a gas, molecular polarization, spectral series.
Q	Heat of vaporization, work done on an atom to give ions.
R	Gas constant; Rydberg constant, gyromagnetic ratio; electrical resistance; molecular refraction, term multiplicity.
S	Spin quantum number; heat of sublimation; spectral series; entropy.
T	Kinetic energy; absolute temperature
U	Lattice energy.
V	Electric potential; energy in volts; potential difference; inner potential of metal; molecular volume; volume of a gas; number of valency bonds; heat of formation of a vapour from gas ions.
V_0	Zero volume.
W	Heat of hydration; work done; probability of a state; negative energy of electron orbit.
X	Magnetic susceptibility.
Z	Atomic number.
Z_e	Effective nuclear charge.

a	Constant for spectral series; van der Waals' constant; amplitude of simple harmonic motion; atomic radius (a_0 or a_H for hydrogen atom); any constant quantity.
b	Number of Bohr magnetons; van der Waals' constant; amplitude of simple harmonic motion; any constant quantity.
c	Velocity of light *in vacuo*; any constant quantity.
d	Molecular diameter; distance between unlike centres in crystals; density of liquid or medium, symbol for electron of a 10-group.
e	Electronic charge; electric charge; base of natural logarithms.
f	Fractional number of molecules per c.c.; electric force; symbol for electron of a 14-group.
g	Landé's splitting factor; group velocity of waves.
h	Planck's constant.

Symbol	
i	Symbol for $(-1)^{\frac{1}{2}}$; chemical constant.
j	Inner quantum number (electron).
k	Mechanical equivalent of heat; azimuthal quantum number; Boltzmann constant; any constant quantity.
l	Serial quantum number (electron).
m	Mass of a body; magnetic quantum number; reduced mass of electron and nucleus; attraction exponent; electric moment; molecular magnetic moment resolved along field axis; induced moment of a molecule "current" number of line series; absolute weight of a molecule.
m_e	Electronic mass.
m_l	Orbital magnetic quantum number
m_s	Spin magnetic quantum number
n	Principal quantum number; index of refraction; repulsion exponent; number of molecules of gas per gram or per c.c.; number of electrons in an ion.
n_e	Effective quantum number.
n_r	Radial quantum number.
o	Angular velocity of orbital precession.
p	Angular momentum; number of electron pairs; number of atoms in unit group of crystal; Weiss magneton number; probability; symbol for electron of a 6-group.
q	Heat absorbed; space moved through; Dirac number.
r	Internuclear distance; radius; index of refraction; polar co-ordinate.
r_e	Equilibrium distance between nuclei.
s	Spin quantum number of electron; dipole distance of induced electric moment; symbol for electron of a 2-group.
s_n	Spin quantum number of nucleus.
s_p	Shielding constant.
t	Dipole distance of permanent electric moment; time; temperature (°C).
u	Ionic mobility; wave velocity.
v	Valency; number of valency electrons; velocity of particle; vibrational quantum number.
v_n	Homopolar valency.
v_p	Polar valency.
w	Wave-number of spectroscopic line.
x	Number of charges carried by dipole; constant of vibrational bands; any unknown quantity.
y	Constant of vibrational bands.
z	Effective atomic number; number of outer electrons.

Symbol	
M	Magnetic quantum number; constant of rotational fine structure of electronic bands; molecular weight.
N	Avogadro number; frequency of revolution; periodic group number; Weiss molecular field constant.
O	Optical representation of energy level.
P	Vapour pressure; parachor; pressure of a gas; molecular polarization; spectral series.
Q	Heat of vaporization, work done on an atom to give ions.
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V	Electric potential; energy in volts; potential difference, inner potential of metal; molecular volume; volume of a gas; number of valency bonds; heat of formation of a vapour from gas ions.
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W	Heat of hydration, work done; probability of a state; negative energy of electron orbit.
X	Magnetic susceptibility.
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a	Constant for spectral series; van der Waals' constant; amplitude of simple harmonic motion; atomic radius (a_0 or a_H for hydrogen atom); any constant quantity.
b	Number of Bohr magnetons; van der Waals' constant; amplitude of simple harmonic motion; any constant quantity.
c	Velocity of light *in vacuo;* any constant quantity.
d	Molecular diameter; distance between unlike centres in crystals; density of liquid or medium; symbol for electron of a 10-group.
e	Electronic charge; electric charge; base of natural logarithms.
f	Fractional number of molecules per c.c.; electric force; symbol for electron of a 14-group.
g	Landé's splitting factor; group velocity of waves.
h	Planck's constant.

Symbol	
i	Symbol for $(-1)^{\frac{1}{2}}$; chemical constant.
j	Inner quantum number (electron).
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l	Serial quantum number (electron).
m	Mass of a body; magnetic quantum number; reduced mass of electron and nucleus; attraction exponent; electric moment; molecular magnetic moment resolved along field axis; induced moment of a molecule "current" number of line series; absolute weight of a molecule.
m_e	Electronic mass.
m_l	Orbital magnetic quantum number.
m_s	Spin magnetic quantum number.
n	Principal quantum number; index of refraction; repulsion exponent; number of molecules of gas per gram or per c.c.; number of electrons in an ion.
n_e	Effective quantum number.
n_r	Radial quantum number.
o	Angular velocity of orbital precession.
p	Angular momentum; number of electron pairs; number of atoms in unit group of crystal; Weiss magneton number; probability; symbol for electron of a 6-group.
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r	Internuclear distance; radius; index of refraction; polar co-ordinate.
r_e	Equilibrium distance between nuclei.
s	Spin quantum number of electron; dipole distance of induced electric moment; symbol for electron of a 2-group.
s_n	Spin quantum number of nucleus.
s_p	Shielding constant.
t	Dipole distance of permanent electric moment; time; temperature (°C).
u	Ionic mobility; wave velocity.
v	Valency; number of valency electrons; velocity of particle; vibrational quantum number.
v_n	Homopolar valency.
v_p	Polar valency.
w	Wave-number of spectroscopic line.
x	Number of charges carried by dipole, constant of vibrational bands; any unknown quantity.
y	Constant of vibrational bands.
z	Effective atomic number; number of outer electrons.

Symbol	
Λ	Absolute value of orbital quantum number of molecule along nuclear line ; wave-length of an electron inside a crystal.
Π	Specific polarization.
Σ, Π, Δ	Spectral series of molecules.
Φ	Eigenfunction.
χ	Magnetic susceptibility.
Ψ	Space-filling constant ; eigenfunction.
Ω	Real volume of molecules in one gram-molecule of gas ; inner quantum number of molecule.

α	Polarizability ; deformability ; degree of ionization ; spin eigenfunction.
β	In relativity theory, v/c; coefficient of compressibility.
γ	Coefficient of expansion.
δ	Lattice distance ; symbol for molecular electron.
ϵ	Dielectric constant ; unit quantum ; phase constant of wave motion ; eccentricity of ellipse.
η	Viscosity coefficient
θ	Angle , polar co-ordinate.
κ	Specific inductive capacity.
λ	Wave-length ; absolute value of orbital quantum number of electron in molecule along nuclear line ; electrical conductivity.
μ	Intrinsic molecular magnetic moment ; total molecular electric moment ; magnetic permeability ; reduced mass of two nuclei , 10^{-4} cm ; quantum defect.
ν	Frequency of spectroscopic line.
ρ	Radius ratio ; r/r_e.
π	Ratio of circumference to diameter of circle ; molecular electron.
σ	Shielding constant (also s_p) ; magnetic moment per gram-molecule ; saturation moment ; surface tension ; surface charge density ; constant in theory of electron scattering ; molecular electron.
τ	Harmonic component in wave theory.
ω	Angular velocity ; vibrational frequency.
ω_e	Equilibrium vibrational frequency.

LIST OF ABBREVIATIONS USED IN REFERENCES

Notes.—The reference numbers in the text appear raised above the type: thus [25] indicates "reference number 25" in the list at the end of the chapter in question Cross-references between different volumes take the form: Vol 3: 37B, which indicates "section 37, sub-section B of Volume 3" In the reference lists, the Journal is first quoted, as in the reference list below, next the year of publication, then the volume and first and last pages. Thus *Z.E.*, 1925, 31, 417–423 means that the paper is in the "*Zeitschrift fur Elektrochemie* for 1925, Volume 31, pages 417 to 423." If the journal is such that it is occasionally renumbered from 1 with a new series number, the latter is placed first in small Roman figures: thus (vii.) 8 means "volume 8 of series number 7." If more than one number of a journal bears the same volume number, then a figure in brackets after the volume number shows this: thus *37* (2) means "the second volume in order of appearance bearing the volume number 37."

A.	*British Chemical Abstracts* (A. Pure Chemistry).
A.C.J.	*American Chemical Journal.*
A.C.P.	*Annales de Chimie et de Physique.*
A.E.S.	*Transactions of the American Electrochemical Society.*
A.F Q.	*Anales de la Sociedad Espanola Fisica y Quimica.*
A.I.M.	*Memorie della Reale Accademia d'Italia.*
A.J.	*Astrophysical Journal.*
A.J.S.	*American Journal of Science.*
A.L.A.	*Atti delle Reale Accademia Nazionale dei Lincei.*
A.P.	*Annalen der Physik* (*Wiedemann's Annalen*, 1877–1899).
A.P.B.	*Bulletin International de l'Academie Polonaise des Sciences et des Lettres.*
A.P.(F.)	*Annales de Physique.*
A.P.P.	*Acta Physica Polonica.*
A.R.	*Annual Reports of the Progress of Chemistry.*
A.S.	*Sammlung Chemischer und chemisch-technischer Vortrage* (*Ahrens*).

LIST OF ABBREVIATIONS

A.S.B.	*Annales de la Société Scientifique de Bruxelles.*
A.S.I.	*Bulletin of the Academy of Science of the United Provinces of Agra and Oudh. Allahabad.*
A.T.M.	*Archiv fur technische Messen.*
A.W.W.B.	See *W.B.*
B.	*Berichte de Deutschen chemischen Gesellschaft.*
B.A.	See *A S.I.*
B.A.R.	*Report of the British Association.*
B B S.	*Bureau of Standards (Washington).*
B.C.S.J.	*Bulletin of the Chemical Society of Japan.*
B.J R.	*British Journal of Radiology.*
B.N.C.	*Bulletin of the National Research Council.*
B.T.J.	*The Bell System Technical Journal.*
C.	*Transactions of the Royal Society of Canada.*
C.B.	*Bulletin de la Société chimique Belgique.*
C.I.	*Chemistry and Industry.*
C.J.R.	*Canadian Journal of Research.*
C.L.	*Communications from the Physical Laboratory of the University of Leiden.*
C.P.J.	*Journal of Chemical Physics.*
C.R	*Chemical Reviews.*
C.Z.	*Chemiker Zeitung.*
D.P.	*Die Physik.*
F.	*Transactions of the Faraday Society.*
G.	*Gazzetta chimica italiana.*
H.	*Helvetica Chimica Acta.*
H.P.A.	*Helvetica Physica Acta.*
I.A.P.	*Proceedings of the Indian Academy of Science.*
I.E.C.	*Industrial and Engineering Chemistry* (Analytical Edition since 1929).
I.J.P.	*Indian Journal of Physics.*
J.A.C.S.	*Journal of the American Chemical Society.*
J.C.P.	*Journal de Chimie physique.*
J.C.S.	*Journal of the Chemical Society.*
J.E.	*Jahrbuch der Radioaktivität und Elektronik* (see *P. Z.*)
J.F.I.	*Journal of the Franklin Institute.*
J.J.P.	*Japanese Journal of Physics.*
J.M.	*Journal of the Institute of Metals.*
J.O.S.	*Journal of the Optical Society of America.*

J.P.	*Journal für praktische Chemie.*
J.P.C.	*Journal of Physical Chemistry.*
J.R.	*Le Journal de Physique et le Radium* (*Journal de Physique* prior to 1920).
J.S.C.I.	*Journal of the Society of Chemical Industry.*
J.S.G.T.	*Journal of the Society of Glass Technology.*
J.T.I.	*The Journal of the Textile Institute.*
J.W.	*Journal of the Washington Academy of Sciences.*
K.B.	*Kolloidchemische Beihefte*
K.C S.M.	*Memoirs of the College of Science, Kyoto Imperial University.*
K.M.G S.	*Arkiv for Kemi, Mineralogi och Geologie* (Stockholm).
K.Z	*Kolloid-Zeitschrift.*
L.	*Liebig's Annalen der Chemie.*
M	*Monatshefte fur Chemie.*
M.M.	*Mineralogical Magazine.*
N.	*Nature.*
N.C.	*Il Nuovo Cimento* (Bologna).
N.G.T.	*Norsk Geologisk Tidschrift.*
N.W.	*Naturwissenschaften.*
O.	*Observatory.*
P.	*Recueil des Travaux chimiques des Pays-Bas et de la Belgique.*
Pa.	*Physica.*
P.A.S.I.	See *I.A.P.*
P.A.T.	*Proceedings of the Imperial Academy* (*Tokyo*).
P.A.W.A.	*Proceedings d. Koninklijke Akademie van Wetenschappen te Amsterdam.*
P.C.P.S.	*Proceedings of the Cambridge Philosophical Society.*
P.C.R.T.	*Scientific Papers of the Institute of Physical and Chemical Research* (*Tokyo*).
Ph.	*Physics.*
P.I.A.	*Proceedings of the Indian Association for the Cultivation of Science.*
P.I.A.T.	*Proceedings of the Imperial Academy* (Tokyo).
P.L.P.S.	*Proceedings of the Leeds Philosophical and Literary Society* (*Scientific section*).
P.M.	*The London, Edinburgh and Dublin Philosophical Magazine.*

P.M.S.J.	*Proceedings of the Physico-Mathematical Society of Japan.*
P.N.A.	*Proceedings of the National Academy of Sciences.*
P.P.S.	*The Proceedings of the Physical Society.*
P.R.	*The Physical Review.*
P.R. (*Supp.*)	*Physical Review Supplement* (becomes *R.M.P.* after Volume I).
P.R.S.	*Proceedings of the Royal Society.*
P.R.S.E.	*Proceedings of the Royal Society of Edinburgh.*
P.T.	*Philosophical Transactions of the Royal Society of London.*
P.Z.	*Physikalische Zeitschrift* (contains *J.E.* since 1924).
P.Z.S.	*Physikalische Zeitschrift der Sowjetunion.*
R.	*Comptes Rendus hebdomadaires des séances de l'académie des sciences.*
Ra.	*Radiology.*
R.M.P.	*Reviews of Modern Physics.*
S.	*Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.*
S.C.	*Science.*
S.E.	*Stahl und Eisen.*
S.F.	*Societas Scientairum Fennicæ, Acta et Commentationes* (Finland).
S.P.	*Science Progress.*
S.R.T.	*Science Reports of the Tokyo Bunriko Daigaku.*
T.	*Scientific and Technology Reports of the Tohoku Imperial University.*
T.H.	*Science Reports of the National Tsing Hua University* (*Series A*).
T.O.C.	*Transactions of the Optical Society.*
U.	*Nova Acta Regiæ Societatis Scientiarum Upsalensis.*
V.	*Verhanalungen der Deutschen Physikalischen Gesellschaft.*
V.K.A.	*Verschlagen d. Koninklijke Akademie van Wetenschappen te Amsterdam* (see *P.A.W.A.*).
W.B.	*Sitzungsberichte der Akademie der Wissenschaften in Wien.*
Z.A.	*Zeitschrift für anorganische und allgemeine Chemie.*
Z.A.P.	*Zeitschrift für Astrophysik.*

Zeitschrift für Elektrochemie.
Zeitschrift für Geophysik.
Zeitschrift für Kristallographie.
Zeitschrift fur Metallkunde.
Zeitschrift für Physik.
Zeitschrift fur physikalische Chemie.
Zeitschrift für technische Physik.
Zeitschrift fur angewandte Chemie (*Angewandte Chemie* since 1932).
Zeitschrift für wissenschaftliche Photographie.

It is well known that no science develops systematically according to a definite preconceived plan, but that its development depends upon practical considerations, and proceeds more or less simultaneously along different lines, corresponding to the many ways of looking at the problems, and to the time and views of the investigator. . . . It frequently happens that theories are found to be interrelated which were started from essentially different view-points; theories, when extended and completed, turn out to be similar and begin to influence one another, appearing helpful or inimical according to circumstances.

Max Planck, in *A Survey of Physics* (Methuen, 1925).

THE FINE STRUCTURE OF MATTER

PART II

MOLECULAR POLARIZATION

CHAPTER X

DIELECTRIC CONSTANTS

26. General Theory: the Dielectric Constants of Gases

IDEAL dielectrics are characterized by a possibility of attaining and maintaining a state of electric stress without any continuous supply of energy from outside sources, and differ in this respect from ideal conductors. There exists, however, no sharp line of demarcation between conductors and non-conductors, and the two types of substance merge continuously into each other. In practice, therefore, dielectrics must be regarded as permitting the passage of an extremely minute electric current.

Meissner[1] has asked: " What is an insulator ? " and concluded that insulating materials contain positive and negative ions close together, with strong bonds between them. Guében[2] has suggested that the current in a dielectric is due to dipoles as well as ions. The electrostatic field in dielectrics is treated mathematically by Wessel.[3]

According to Coulomb's law, the force between two charges of magnitude e and e' concentrated at a distance r centimetres apart is proportional to ee'/r^2, and is given by

$$f = \frac{1}{\epsilon}.\frac{ee'}{r^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where ϵ is the " dielectric constant," referring to the medium in which the charges are placed. The dielectric constant of a medium may be measured by the ratio between the capacity of a condenser having the given dielectric separating the plates and that of the same condenser when the dielectric is air. The dielectric constants of gases are not far removed from the value unity.

The force F exerted at a point where a *unit* charge is situated by a charge e at distance r from it is given by putting $e' = 1$ in the expression of equation (1), so that

$$F = \frac{e}{\epsilon r^2} \quad \text{.......................} \quad (2)$$

and $F = f/e'$. This force is a measure of the strength of electric field, or of the " electric intensity " at the point in question. Moreover, the surface density of charge σ at distance r induced on a conductor by a charge e is given by

$$\sigma = \frac{e}{4\pi r^2} = \frac{\epsilon}{4\pi} \cdot \frac{e}{\epsilon r^2} = \frac{\epsilon F}{4\pi} \quad \text{...............} \quad (3)$$

It may be added that the quantity of energy per unit volume in an electrified dielectric is given by the expression $\epsilon F^2/8\pi$.

The dielectric constant of a medium varies for different wave-lengths of radiation passing through it, and approaches a limiting value corresponding to infinite wave-length and zero frequency. This value is usually quoted in tables, and is obtained by extrapolation of measurements. An advantage of referring ϵ to zero frequency is that the number obtained is applicable to " static " fields, such as are set up between the plates of charged condensers.

According to the Clausius-Mosotti rule, the quantity $(\epsilon - 1)/d(\epsilon + 2)$ is a constant independent of temperature, d being the density of the medium. Actually, wide divergences from the rule are often found, a discussion of which follows later. " Molecular polarization " P is defined by the relation :

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} \quad \text{.......................} \quad (4)$$

where M is the molecular weight of the substance (see this vol. : 29).

Maxwell deduced from the electromagnetic theory of light :

$$\epsilon = r_{\infty}^2 \quad \text{..............................} \quad (5)$$

where r_∞ is the refractive index of the medium for light extrapolated to infinite wave-length. Within the limits of applicability of this relation, combining equations (4) and (5), the " molecular refraction " R may be written :

$$R = \frac{r_\infty^2 - 1}{r_\infty^2 + 2} \cdot \frac{M}{d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

This is the Lorenz-Lorentz relation. Complicating facts in studying the applicability of the above relations are : (1) both ϵ and r vary with wave-length of radiation employed ; (2) P is not generally independent of temperature. These matters are considered below.

Methods of determining dielectric constants have been summarized by Blüh.[4]

In the case of gases, dielectric constants do not vary very much from the value unity, so that equation (4) becomes very approximately

$$P = \frac{\epsilon - 1}{3} \cdot \frac{M}{d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

$(\epsilon - 1)/d$ being sometimes called the Newton function. If P is to remain constant with changing pressure (or density), $\epsilon - 1$ must be proportional to d. Now the function should also be independent of temperature, but this is not generally true. The failure of the older theory in this respect led Debye to state the theory of polar molecules, according to which (see this Vol. : 30c)

$$P = a + \frac{b}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

where T is the absolute temperature, and a, b are constants having special significance. This theory is treated in the sequel. Equation (8) may be written in the form $PT = aT + b$, or $b = T(P - a)$, PT being linear with T.

Jona[5] verified this result of the Debye theory in the cases of air, CO_2, NH_3, SO_2 and the vapours of CH_3OH and H_2O over varying temperature ranges up to about 450°K. Satisfactory agreement was found, except where gases were at temperatures near the liquefying points, marked rises in PT being observed in the cases of H_2O, CH_3OH and SO_2 (see Figures LX and LXI) This anomaly was attributed by Jona to association Further work in establishing the validity of a relation of the type (8) has been carried out by Weigt[6] on CO and CO_2, by Compton and Zahn[7] on HCl, HBr and HI, and by Stuart[8] on air, CO_2, and the vapours of methyl and ethyl ethers, ethylene oxide and acetone,

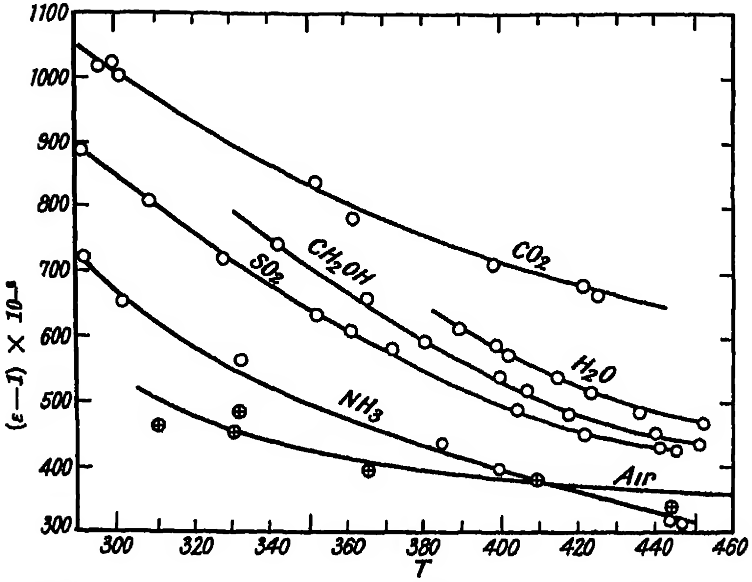


FIGURE LX —VARIATION OF ε–1 WITH TEMPERATURE FOR GASES (JONA)

the last-named between room temperatures and 180°C. In each case, the variation of $\epsilon - 1$ with T shows a smooth curve, the dielectric constant falling with rising temperature as predicted by the theory

The Clausius-Mosotti relation was found to hold good by Tangl[9] in respect of changes of pressure in air, H_2 and N_2 between 20 and 100 atmospheres, and by Occhialini and Bodareu[10] for air up to 350 atmospheres The dielectric constants increased with pressure, as required by the Clausius-Mosotti and Newton relations Further work was carried out by Riegger[11] on air, H_2, CH_4, CO_2 and CO over a pressure range 400 mm to 760 mm, and by Waibel[12] on air between 1 and 40 atmospheres The results yielded almost perfectly constant values of the functions (4) and (7) over the ranges studied

Zahn[13] determined the dielectric constant of water vapour between 3 and 20 mm pressure and over a temperature range 23° to 165°C At room temperature, the curve connecting $\epsilon - 1$ with pressure was found to consist of two straight parts connected by a curved portion giving a change of slope This irregularity tended to disappear at higher temperatures, and Zahn explained it by adsorption, which increased with pressure, of water molecules on the condenser plates during the determination, leading to increased capacity and dielectric constant It was suggested that the irregularities observed by Jona near the temperature of condensation might be similarly explained Wolf[14] found linear relations between $\epsilon - 1$ and pressure for CO_2, N_2, O_2 and H_2 between 1,200 mm down to very low

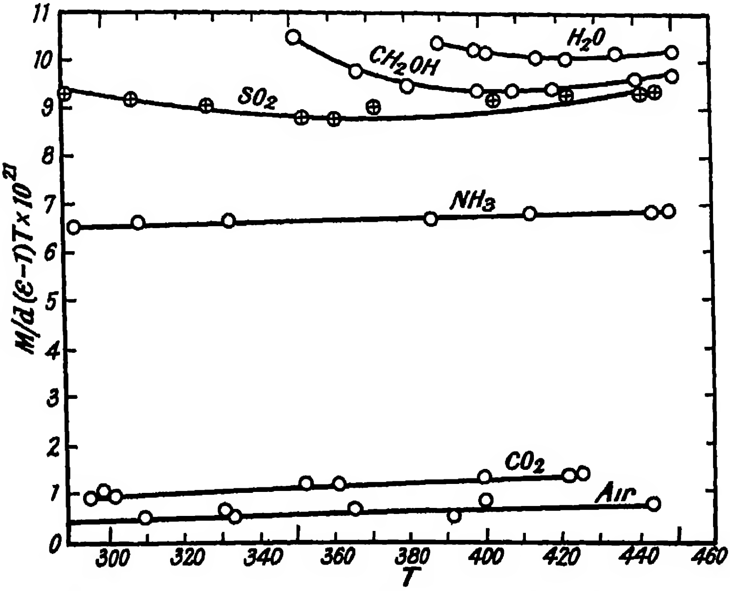


FIGURE LXI—VARIATION OF *PT* WITH *T* FOR GASES pressures, whilst for H_2O and NH_3 curves of the type described by Zahn were obtained The effect of altering the distance between the condenser plates was studied The results were somewhat unfavourable to Zahn's adsorption hypothesis

The ϵ of N_2[15] is found to give a constant Clausius-Mosotti function from 1 to 1,000 atmospheres pressure and from 25° to 150°C An earlier observation[16] showed that the ϵ of dry, dust-free air increased linearly with pressure, up to 170 atmospheres On the other hand, CO_2[17,18,38] and NH_3[10,38] showed small changes in the Clausius-Mosotti function at high pressures Keyes and Kirkwood[18,19] suggested that the relation was only applicable to the case of infinitely low density, and proposed a modified formula (see this vol 29)

Recent measurements have been made on the following: He,[20] Ne,[20,21] A,[20,21] Kr,[20] Xe,[20] H_2,[20] O_2,[20] N_2,[15,22,23,24,25] air,[16,22] CO_2,[17,18,20,22] N_2O,[22,26,40] NO,[22] CO,[22] NH_3,[10] SiH_4,[22] Si_2H_6,[22] SF_6,[22] SiF_6,[22] CS_2,[26,39] CH_4,[22] C_2H_6,[22] C_3H_8,[22] C_6H_{14},[37] C_7H_{16},[37] C_2H_4,[22] C_2H_2,[22] $C_2H_4Cl_2$,[27] $C_2H_4Br_2$,[27] and CH_3COOH [271] Metallic vapours were examined by Kruger and Maske [28]

Strong electric and magnetic fields[29] are found to have no effect on the ϵ's of He (20 cm pressure), air and O_2 (normal pressure) The zero influence of strong magnetic fields has been confirmed for A,[31] O_2,[30,31] H_2,[30] CO_2[30] and N_2.[30]

Methods of calculating ϵ's have been applied to He,[32,33] A,[33] HF,[34] F_2,[34] Cl_2,[34] Br_2[34] and I_2 [34] A linear relationship[35] is found between $\log(\epsilon^{-1})$ and the ionization potentials of the inert gases.

The energy associated with explosive mixtures of CO and O_2[36] has been determined by the dielectric strength (D.S.) of the gaseous medium It is found that drying with P_2O_5 increases D S , small amounts H_2O at first reduce and then increase D.S., whilst addition of H_2 reduces D S The capacity component, however, is not necessarily responsible for ignition,[41] and Smithells and co-workers[42] were justified in concluding that H_2 is more effective than H_2O in increasing the sensitivity towards ignition of $2CO + O_2$ mixtures

27 The Dielectric Constants of Liquids

(A) **Pure Liquids** (a) *Inorganic Substances* The change of the dielectric constant of ***water*** with wave-length has been studied by a number of observers [43,44,45,46,47,48,49] The value for long waves is very approximately 79 Lili Kockel[50] estimated the changes of dielectric constant of water with temperature, and derived a continuously falling curve between 0° and 100°C The variation was not found to agree with the Debye formula (8), PT being not linear with T Although rather better agreement was obtained with another formula due to Gans, the matter does not appear to have been very satisfactorily explained More recent work is due to Astin,[51] Cuthbertson, Linton and Maass,[52,55] and others [53,54]

Other inorganic substances studied are H_2O_2,[56] N_2H_4,[57] Br_2,[58] liquid S[59,60] and P [61]

Work has also been carried out on the dielectric constants of liquefied gases Thus Wachsmuth[73] records the following results of Messtorff on liquid ***oxygen***, ***nitrogen*** and ***air*** respectively $\epsilon = 1\ 51$, $1\ 58$ and $1\ 56$ Ebert and Keesom[74] investigated the dielectric constant of liquid ***nitrogen*** over the temperature range 63 9 to 76 5°K, and found that the Maxwell and Clausius-Mosotti relations were valid Work has been done on the dielectric constants of liquid ***oxygen***, ***hydrogen*** and ***helium*** in the laboratory of Kamerlingh-Onnes For liquid oxygen, over the temperature range 90 3 to 70 8°K, the dielectric constant varied from 1 145 to 1 239, and the Clausius-Mosotti function $P/M = (\epsilon - 1)/(\epsilon + 2)d$ between the limits 0 1167 and 0 1173 For liquid hydrogen, over the range 20 4 to 14 4°K, the dielectric constant varied from 1 211 to 1 236, and the Clausius-Mosotti function from 0 928 to 0 951 The pressure was steadily decreased over the ranges named For liquid ***helium***, a dielectric constant of 1 048 at 765 mm pressure was obtained Further more recent work has been carried out on ***hydrogen chloride***,[62] ***nitrogen***,[63] ***argon***,[63] ***methane***[63] and ***nitrous oxide*** [63]

(b) *Organic Substances* Ratz[75] calculated the temperature coefficient of dielectric constant of a large number of organic liquids, and Abegg and Seitz[76] found a rapid increase in dielectric constant with temperature in the cases of *toluene*, *ether*, *acetone* and *amyl* and *ethyl alcohols*, the values of ϵ conforming approximately with the relation $\epsilon = c\,e^{-\frac{T}{190}}$, where c is a constant A sudden fall in dielectric constant was found to occur on solidification, an observation confirmed by other

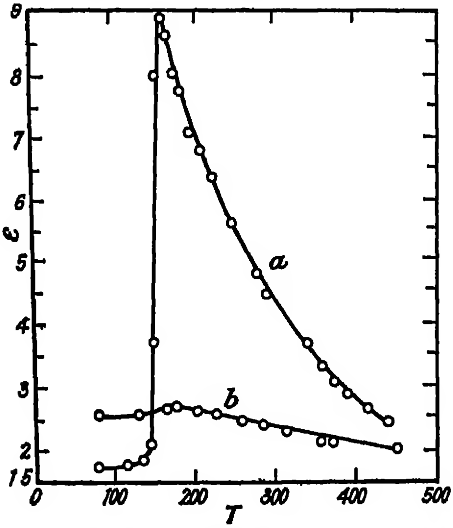


FIGURE LXII —VARIATION OF DIELECTRIC CONSTANT ϵ OF (a) ETHER, (b) TOLUENE, WITH TEMPERATURE

workers Isnardi and Gans[77] found that the dielectric constant of *ethyl ether* rose to a maximum value at −108°C, below which it fell rapidly to a constant value for the solid state A somewhat different curve was obtained for *toluene* (Figure LXII) In the case of ether, the Clausius-Mosotti function was not constant, but $PT/M = (\epsilon - 1)T/(\epsilon + 2)d$ was found to be linear with T, as the Debye equation requires This is shown in Figure LXIII, which may be contrasted with Figure LXIV, where the Clausius-Mosotti function is found to be practically constant in the liquid state for toluene, the PT curve being linear with T, and, when extrapolated, passing through the origin These figures clearly show the difference in behaviour between polar ether and practically non-polar toluene in respect

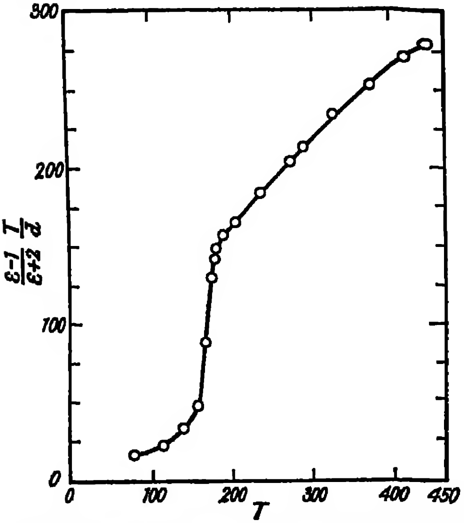


FIGURE LXIII — VARIATION OF POLARIZATION OF ETHER WITH TEMPERATURE

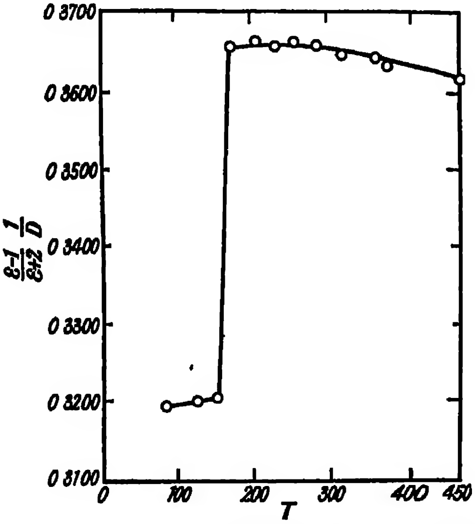


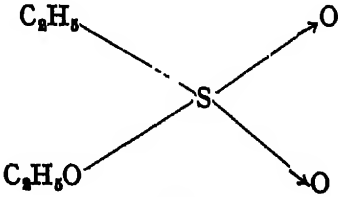
FIGURE LXIV — VARIATION OF POLARIZATION OF TOLUENE WITH TEMPERATURE

of changes of ϵ with temperature Using Abegg and Seitz's results, Isnardi and Gans found that the Debye condition was fulfilled for *methyl* and *ethyl alcohols* between +10° and −100°C Polar *chloroform* gave results similar to ether, and *carbon tetrachloride, benzene, m-xylol* behaved as non-polar like toluene The meaning of these results is most easily interpreted in the light of the Debye theory (see this vol 30C)

Herz[78] collected a large amount of information respecting the values of the Clausius-Mosotti and Lorenz-Lorentz functions for a large number of organic liquids It was found that P was approximately equal to R for many hydrocarbons and for *thiophene*, where the Maxwell relation was obeyed In the cases of most organic chlorides, bromides and iodides, esters, acids, alcohols and amines, the P/R ratio departs widely from the value unity In homologous series, the ratio tends to decrease with increasing carbon content

Walden[79] measured the dielectric constants of 60 purified solvents for a series of different temperatures, and found that the Clausius-Mosotti function was not constant and varied with temperature Liquids having high dielectric constants were found to contain " dielectrophore " groups in their molecules, the groups being mainly negative in chemical character, as in the following cases $-OH$, $-NO_2$, $-CN$, $-SCN$, $-NCS$, $-NH_2$, $-F$, $-Cl$, $-Br$, $-I$, $=CO$ and $=SO_2$ In order to obtain a high dielectric constant, these groups must be combined with others called " dielectrogene," prominent amongst which are $-H$ and the alkyl groups CH_3, C_2H_5, C_6H_5 When dielectrophore groups are combined together, the dielectric constant is low, as in liquid Cl_2, Br_2 and C_2N_2

An increase in polarity of a molecule is generally associated with increase in dielectric constant This is also found to accompany the introduction of " semi-polar " bonds into molecular structure Thus, for diethylsulphite $(C_2H_5O)_2S \rightarrow O$, where one semi-polar bond occurs, $\epsilon = 16$, whilst for ethyl ethyl sulphinate



where two semi-polar bonds are present, ε = 42 The presence of polarity may, however, result in molecular association in such a way that the dielectric constant is lowered This is a secondary effect (see this vol 40)

Walden and Werner[60] observed a difference in the dielectric constants of *cis*- and *trans*-dichloroethylenes (CHCl CHCl) The results recorded for room temperature (about 16°C) were *cis*-compound, ε = 3·67 , *trans*-compound, ε = 7·55 Errera and Lepingle[61] found the values at 20°C *cis*-compound, ε = 9·22 , *trans*-compound, ε = 2·25 The order of dielectric constants is thus reversed Errera[62] discussed the isomers of CHCl CHI, the positions of the atoms in the two geometrical isomerides having been determined by van de Walle and Henne The iodine atom appears to be relatively positively charged in relation to the chlorine atom in the molecule, the dipole moment of the *trans*-compound in dilute benzene solution being found to be more than twice that of the *cis*-compound The moment is increased by increasing the distance between the unlike charges

Further more recent work has been carried out on the following organic compounds *pentane*,[65] *hexane*,[65,66,67] *heptane*,[65] *octane*,[65] *nonane*,[65] *decane*,[65] *undecane*,[65] *dodecane* ,[65] *ethyl ether*,[52,55,57,68] *n*- and *iso-propyl ethers*,[68] *methyl ethyl ketone* ,[57] *methyl chloride*,[57] *chloroform*,[66,67] *methyl cyanide*,[57] *methylamine*,[57] *ethylamine*,[57] *urethane*,[57] *monochloracetic acid* ,[57] *methyl alcohol*,[57] *ethyl alcohol*,[70] *n*- and *iso-propyl alcohols*,[70] *n*- and *iso-butyl alcohols*,[66,69,70] *dimethyl ethyl carbinol*,[66] *amyl alcohol* ,[70] *oxalyl chloride*,[68] *dioxan*,[57] *ethylene dichloride*,[55,57,71] *ethylene glycol*,[69] *propylene chloride*,[68] *acetal*,[66,67] *ethyl behenate* ,[72] *benzene*,[51,52,55,64,66,67,68,71] *nitrobenzene*,[52,55,66,68,70,71] *benzonitrile*,[66,71] *chlorobenzene*,[52,57,70,71] *phenol*,[57] *o*-, *m*- and *p-xylenes*,[68] *o-nitrotoluene*,[66] *o-methylnitrobenzoate*,[68] *acetophenone*,[71] *cinnamic aldehyde*,[68] *quinoline*,[70] and *methyl cyclohexane* [68]

(c) *Influence of Conditions* Many investigations have been carried out on the effect of pressure on the dielectric constants of liquids[63] Kyropoulos[64] used pressures up to 3,000 kg /cm^2, and found that whilst ε diminished with increasing pressure for *ether, carbon tetrachloride, ethyl* and *methyl alcohols* and *water*, the

Clausius-Mosotti function was constant only for the first two named. In the other cases, P decreased with increasing pressure, and this was attributed to the effect of association which tended to increase the number of complexes having smaller moment than the unassociated molecules. Danforth[85] has measured the dielectric constants of ten liquids for pressures up to 12,000 atmospheres. Whilst in many cases the reciprocal of the Clausius-Mosotti function varied linearly with density, it was found that the relations in the cases of *carbon disulphide*, *pentane* and *ethyl ether* were more complicated.

Malsch[86] detected no change in the dielectric constants of *water*, *glycerine* and *ether*, using fields of intensity 100,000 volts/cm. This result was not in accord with the Debye theory. In a further investigation, using an improved method, the same observer[87] found small but appreciable diminutions in ϵ at 250,000 volts/cm, amounting to 0·7%, 1·0% and 1·5% for *water*, *nitrobenzene* and *ethyl alcohol* respectively. Allowance being made for the effect of association, the results were found to be in agreement with the Debye theory. Kautzsch[88] studied the variation in ϵ with changing electrostatic fields, and used the results to calculate the dipole moments of *ether*, *chloroform* and *chlorobenzene*. Saturation effects were observed in the cases of the first two named. Gundermann[89] has reviewed the work on the effect of field strength, and has confirmed that the dielectric constants of liquids fall with field strength, and finds them to be diminished proportionally to the square of the applied field, as the Debye theory requires.

Lunt and Rau[90] have found that the dielectric constants of *benzene*, *ether* and *chloroform* do not vary with frequency from 1 to 1,000 kilocycles per second. In the cases of *ethyl alcohol*, *acetone*, *aniline* and *nitrobenzene*, a slight increase was observed between 100 and 1,000 kilocycles per second. For rather longer waves in the neighbourhood of 10^4 to 10^5 kilocycles per second, the Debye theory requires a marked decrease with increasing frequency in the dielectric constant of liquids having dipole moment, accompanied by strong absorption of the electric waves.[91,92] This effect, known as "anomalous dispersion," was first observed by Drude. The absorption is responsible for "dielectric loss," and results in heating the dielectric In the case of a polar liquid, the effect of an alternating field is to orientate the molecular dipoles, but the polarization due to the orientation reaches its maximum value τ seconds later than the field, where τ is the "relaxion time," of the order 10^{-12} sec The theory, so far as it has been worked out by Debye, leads to the conclusion that the polarization formula (see this vol 30C) must be modified in such a way that the second term (due to permanent dipoles) is divided by $1 + i\omega\tau$, where ω is the number of vibrations in 2π secs Hence the dielectric constant decreases as ω increases, in accordance with observation The relaxion time is given by an expression involving η, the viscosity of the medium (see this vol 31C) The anomalous dispersion occurs at a frequency given by $1/\tau$ [93] Experiment has largely confirmed that non-polar liquids give no dielectric power-loss, whilst polar liquids give heating effects increasing with μ This has been clearly established in the case of the isomeric *dichlorobenzenes* [91] Jackson[94] has investigated power-losses in *benzene, toluene, chlorobenzene* and *nitrobenzene* Evidence of the existence of dipoles in *primary alcohols* has been obtained by Krause[95] by this method

Goss[96] has explained, by application of formulæ due to Raman and Krishnan, the observed slight increase in total polarization of a non-polar liquid with temperature

Piekara and Schérer[97] have shown, in the cases of eight organic liquids, that the dielectric constants increase in magnetic fields of 51,000 gauss

(B) **Liquid Mixtures** Researches considered in this sub-section include cases where the leading interest lies in the determination of ϵ's of liquid mixtures, and the influence of conditions (variation with concentration, temperature, etc) Further cases are treated in this vol 37 Convenient summaries have been provided by Lowry[98] and Lichtenecker [99]

The detailed researches of Williams and collaborators[100] and of Smyth and collaborators[101] may be briefly noted here It is found, in general, that the polarization of a liquid is independent of admixture with non-polar solvents The Debye condition for variation with temperature was found to be valid, for infinite dilution, in the cases of solutions of *chlorobenzene, bromobenzene* and *chloroform* in *hexane* [102]

Many attempts have been made to express the dielectric constant of a liquid mixture in terms of the dielectric constants of the components The general relation takes the form

$$f(\epsilon) = v_1 f(\epsilon_1) + v_2 f(\epsilon_2) \qquad (9)$$

for binary mixtures, where ϵ, ϵ_1 and ϵ_2 are the dielectric constants of the mixture and components 1 and 2 respectively, v_1 and v_2 are the ratios of the volumes of the components to the volume of the mixture, and the same function of the dielectric constants concerned is used throughout, in a given case Thus Silberstein,[103] assuming no change of volume on mixing and no interaction between the constituents, derived a thermodynamic proof of the formula obtained by putting $f(\epsilon) = \epsilon$ in equation (9) The law was found to give satisfactory results in the comparison of calculated and observed dielectric constants of mixtures of *benzene* and *phenyl acetate* Kerr[104] studied organic mixtures conforming to Silberstein's rule, and found certain deviations which were attributed to molecular association Grutzmacher[105] supported Silberstein's assumption by experiments on the mixtures *carbon tetrachloride-carbon disulphide, carbon tetrachloride-chloroform, carbon disulphide-benzene*, and *toluene-benzene* Philip,[106] in the course of an investigation covering a large number of organic mixtures, studied (1) the case $f(\epsilon) = (\epsilon - 1)/(\epsilon + 2)$, using the expression which occurs in the Clausius-Mosotti formula, and (2) the case $f(\epsilon) = \sqrt{\epsilon} - 1$, as in a formula associated with Beer, Landolt and Gladstone (see [98,99,105]) Either formula gave equally satisfactory results where both components of a binary mixture possessed low dielectric constants, as with mixtures of *benzene* and *ether* and of *carbon disulphide* and *chloroform* In other cases, certain discrepancies appeared, especially where alcohols were used as one component, where the pure alcohols and solutions more concentrated in alcohol showed abnormally high values of the dielectric constants as compared with those required by the mixture formulæ Such cases may be linked with the occurrence of molecular association Similar results were obtained by Philip and Haynes[107] in mixtures containing phenols, which are known on cryoscopic grounds to associate in benzene and other solvents (see Philip and Clark[108]) The theory that deviations from the mixture rules may often be attributed to association has been largely confirmed by work, carried out in the light of the Debye theory, as, for example, by Lange,[109] according to which two types of association may occur, having opposite effects on the dielectric polarization Wiener[110] put $f(\epsilon) = (\epsilon - 1)/(\epsilon + u)$, where u assumes various values, such as 0, 2, ϵ, 2ϵ and ∞ For $u = 2$, the formula reduces to that used by Philip (case 1), and for $u = \infty$, to that of Silberstein

More recent work has fully tended to confirm the inapplicability of a formula of the type of equation (9) to general cases Piekara[111,112] studied *water-alcohol* mixtures in *oil*, *mercury* in *oil*, and *mercury* in *vaseline*, and concluded that ideal non-homogeneous mixtures do not obey a linear additivity rule In certain cases, the dielectric constants of liquid mixtures are greater than those of either component this is true of *water-hydrogen peroxide*[56] and *ethyl alcohol-propyl alcohol* mixtures[89] According to Kyropoulos,[113] the mixture rule is never accurately obeyed for example, in *acetone-benzene* mixtures, dissociation of acetone occurs, whilst with mixtures of *methyl alcohol* and *acetone* in *water*, hydration is responsible for variations Ball[66] has studied *toluene-amyl alcohol* mixtures Briegleb[114] reports deviations from additivity for mixtures, as follows *carbon disulphide-heptane*, *carbon disulphide-carbon tetrachloride*, *carbon disulphide-benzene*, and in other cases Howell and Jackson[115] find a nearly linear relation for the mixture *phenol—m-cresol*, whilst deviations are found for *phenol* in *water*, *aniline* and *p-toluidine* Wyman,[116] however, has found the rather unexpected result that the additivity rule holds throughout all ranges of concentration for mixtures of the polar liquids *water* and *ethyl alcohol*

The variation of dielectric constants of liquid mixtures with temperature[117] has been found to be expressible by a formula $\epsilon = ae^{-bt}$, where a, b are constants, in the following cases, *water* being one component *methyl*, *ethyl*, n-*propyl*, *isopropyl*, and *tertiary butyl alcohols*, *ethylene glycol*, *glycerol*, *acetone*, *mannitol* and *cane sugar*

Hiegemann[118] has found the high frequency conductivity of *water-glycerol* mixtures to be inversely proportional to the square of wave-length, as theory requires Haass[119] has studied the anomalous dispersion of *hexyl alcohol* gradually diluted with *benzene*, and finds that the peak maxima shift in the direction of lower wave-lengths with increasing amounts of benzene, the curves becoming at the same time increasingly flattened out *Amyl alcohol* in *benzene* behaves similarly In the work of Krause,[95] previously noticed, it was shown that in the region of anomalous dispersion, mixtures of *butyl alcohol* with *oil*, *oil* and *carbon tetrachloride*, and pure *carbon tetrachloride* respectively showed decreasing frequency corresponding to maximum loss with increasing viscosity of the mixtures, in accordance with the theoretical conclusions made by Debye

Johnstone and Williams[272] examined the variation of ϵ's for solutions of *nitrobenzene* and *p-dinitrobenzene* in *mineral oil* of high viscosity, and found that ϵ decreased with increasing frequency The relaxion time was calculated for nitrobenzene by the Debye formula (see this vol 30C), allowance being made for molecular association The calculation also yielded an estimate for the molecular diameter of the right order of magnitude

(C) **Aqueous Solutions** (a) *Electrolytes* The earlier investigations were conducted on dilute aqueous solutions, with a view to ascertaining whether the dielectric constant of water was raised or lowered by addition of a solute The effects in such solutions were found small in all cases studied, but the evidence proved somewhat conflicting, elevations of dielectric constant being found by Cohn,[120] Nernst[121] and Smale[122] and depressions by Drude[123] and Palmer [124]

More recently, Lattey[125] has found lower dielectric constants in dilute solutions of KCl and $CuSO_4$, and Bluh[126] has deduced on theoretical grounds that the dielectric constants of electrolytic solutions should decrease linearly with increasing conductivity, the assumption being made that departures from the mixture rules may be attributed to hydration of ions   It is found that the experimental values of Sommer (Dissertation, Berlin, 1923) are in qualitative though not in exact quantitative agreement with the theory   Furth,[127] using a new experimental method, finds first a decrease and then an increase in ϵ between 0 and 1% NaCl in water   The minimum is less strongly marked when the potential between the condenser plates is 30 than when it is 15 volts   Zahn[128] reports a lowering of ϵ for concentrated solutions of strong electrolytes, the value for saturated LiCl being smaller than for NaCl solution of the same conductivity

Walden, Ulich and Werner[129] obtained minima in the curves connecting ϵ with concentration for non-aqueous solutions, but for aqueous solutions of KCl, $CdBr_2$, $BaCl_2$ and $N(C_3H_7)_4I$, the ascending parts of the curves were not realized   Hellmann and Zahn[130] have found the increase in dielectric constant with concentrated solutions in water, and that, in the case of certain salts, the dielectric constant of water is exceeded   Aqueous solutions are divided by the authors into two classes   (1) those which at high concentrations show only small lowerings of dielectric constant, and in which the increase at higher concentrations is not proved, as HCl and the alkali halides, and (2) those which show a definite minimum of dielectric constant corresponding to a certain limiting concentration, and which, after passing the minimum, give rapidly-increasing values, as $CuSO_4$ Deubner[131] and Rieckhaff[132] record results in general agreement with those of Hellmann and Zahn   The falling parts of the curves may be associated with ion hydration and the orientation of water dipoles by ions, and the subsequently-increasing values of dielectric constants with more concentrated solutions, leading to values higher than that of pure water in some cases, with the thinning of the water layer around ions due to the decreasing proportion of water molecules

More recent work has shown widely varying observations, as in the case of *aqueous potassium chloride*, where four different results have been reported   (1) Carman and Schmidt[133] found *a minimum* in the curve connecting dielectric constant with concentration   A similar result was obtained by Astin,[51] whilst Milicka and Slama[134] have found minima for 19 different aqueous salts, acids and bases. (2) Drake, Pierce and Dow[53] found that the dielectric constant of aqueous potassium chloride was ***not much affected*** by concentration, and nearly the same as for pure water. (3) Carman and Smith[135] reported for this substance in dilute solution that the dielectric constant first increases above that of pure water, and then decreases, giving ***a maximum***, similar results being found in other cases. (4) Lattey and Davies[136] found ***a constant increase*** with concentration for several salts, including potassium chloride in aqueous solution. Orthmann[137] reported similar results for silver salts. Malone, Ferguson and Case[138] called attention to the generally discrepant nature of the results, and pointed out that the problem was even more complex than had been realized, and that no adequate theoretical treatment had been given to the divergences. The dielectric constants of aqueous solutions appear, however, to be remarkably sensitive to changes in (a) temperature,[135] and (b) frequency,[139] and this may partly be found to account for the discrepancies.

Kossel,[6] in the course of his consideration of chemical electrostatic phenomena, considered the work necessary to separate K^+ from Cl^- in the case of KCl, equal to $e^2/2r$, where e is the electronic charge ($4{\cdot}77 \times 10^{-10}$ E.S. units) and r the distance separating nearest centres in the crystal, taken as 2×10^{-8} cm. This gives $\mathbf{5{\cdot}4 \times 10^{-12}}$ erg. The thermal agitation energy (of three degrees of freedom at 17°C.) is $3RT/2N$ per molecule, where R is the gas constant $= 0{\cdot}8312 \times 10^8$ ergs, N the Avogadro number $= 6 \times 10^{23}$ and T the absolute temperature (290°K.). Substituting these numbers, the molecular thermal agitation energy may be approximated as $\mathbf{5{\cdot}8 \times 10^{-14}}$ erg, which is evidently insufficient to ionize the substance. In water, however, the energy necessary to separate the oppositely-charged ions becomes $e^2/\epsilon\, 2r$, or $\frac{1}{80} \times 5{\cdot}4 \times 10^{-12} = \mathbf{6{\cdot}8 \times 10^{-14}}$ erg, so that the thermal agitation energy becomes of the right order, enabling dissociation to occur. Similar considerations would apply in the case of non-aqueous solvents.

Theoretical treatment of the dispersion of dielectric constants of strong electrolytes in solution, and the relations between conductivity, concentration and dielectric properties, is due to

Debye and Falkenhagen,[140] whose theory is based upon the conception of ionic atmospheres, first suggested by Debye and Huckel The treatment has been extended to mixed solutions of strong electrolytes [141] It would take us too far from our present course to examine these theories in detail, and the general theory of electrolytes will be treated elsewhere It may be noted here that the Debye-Falkenhagen theory has been largely verified by several authors, notably by Zahn,[142] Wien,[143] Ježewski and Kamecki,[144] Plotze,[145] Stips[146] and Henniger [147] Further details will be found in the literature cited

(b) *Non-Electrolytes* Non-electrolytic aqueous solutions have also received their share of attention Harrington[148] investigated ***sugar*** and ***urea*** solutions, following on the investigations of Drude [123,149] Lattey[125] also examined sugar solutions, whilst Kockel[50] studied the temperature variation of sugar and urea solutions Furth,[150] in an important investigation, examined the variation of dielectric constant with concentration in the cases of (1) ***dextrose, lævulose*** and ***cane sugar,*** whose values decreased with increasing concentration and were never greater than that of pure water, (2) ***urea*** and ***glycocoll,*** which showed increasing dielectric constant with increasing concentration, and (3) ***saccharin,*** whose value first increased and then decreased In cases where a rise is noted, this is attributed on the Debye theory to the solute containing a greater number of dipoles per unit weight than the solvent, the subsequent decrease after passing a maximum being associated with the increasing viscosity of the solution. If this maximum falls at zero concentration, the curve relating dielectric constant to concentration will continually decrease due to the viscosity effect, and substances of Furth's type (1) will fall in this class. The same type is obtained where the dipole moment of the solute is less than that of the solvent If the maximum is located at saturation, a continually increasing curve is obtained (Furth's type (2)) If it occurs anywhere else, type (3) above is obtained The results of Furth provide examples of all the types, and illustrate Debye's theory remarkably well The matter will be taken up again in connection with the Debye theory.

Furth and Bluh[151] have investigated amphoteric substances containing " Zwitterions " in aqueous solution, and find in all cases a maximum value in the curve connecting ϵ with concentration, the curves first rising and then falling away Substances examined were *hippuric* and *sulphanilic acids, helianthin,* and ortho- and para-*aminobenzoic acids* *Serums* and other substances of biological interest have been examined by Furth[150] and Keller[152] The dielectric constants of egg albumin solutions have been measured[153]

Devoto[154] measured the dielectric constants of aqueous solutions of *sulphamide* $SO_2(NH_2)_2$, and deduced the polar formula $NH\ SO(NH_3^+)O^-$ For *amino-acids,*[155,156] the dielectric coefficient (rate of increase of ϵ with concentration) increases with increasing length of chain, and is proportional to the corresponding dipole moments Further confirmation of the theory of amphoteric ions has been obtained for *amino-acids,*[157,158] *polypeptides*[157,158] and *gelatin*[159,160]

(D) Non-Aqueous Solutions (a) *Dissolved Gases* Two researches may be noted here Gases dissolved in oils are found to have a marked effect on their dielectric constants,[162] whilst *hydrogen chloride* dissolved in *benzene, cyclohexane* and *carbon tetrachloride* has a higher polarization than in the free gaseous state[163]

(b) *Dissolved Solids* Eggers[164] studied the dielectric constants of solutions of *sulphur* in *carbon disulphide,* and found the values to lie between those of the pure components In other cases examined, this did not hold According to Platzmann,[165] sulphur has a low dielectric constant, and therefore low ionizing power (see below) Rosental[166] has reported that solutions of *sulphur* in *benzene* obey the Clausius-Mosotti law, whilst in *carbon disulphide* a small increase of polarization with temperature occurs Dobinski[167] has determined the dielectric polarization of S in the last-named case as 0 252 cc per gram

Kahlenberg and Anthony[168] have examined solutions of different *metallic oleates* in various solvents It was found that, in general, the dielectric constants of solutions were only slightly less than those of the corresponding pure solvents An interesting fact about these solutions is that the effect of the metal was masked in the observations

Walden[169] reported his investigations of solutions of the salts of *alkyl-substituted ammonium bases* in three solvents *chloroform* ($\epsilon = 4\ 95$), *methylene chloride* ($\epsilon = 8\ 1$) and *ethyl formate* ($\epsilon = 8\ 2$) It was found that the dielectric constants of the solutions were in general much higher than those of the pure solvents and increased with increasing concentration Thus, the dielectric constants of solutions of *tetraethylammonium chloride* in *methylene chloride* at dilutions of 40 and 20 litres were 9 3 and 10 15 respectively The percentage increase in dielectric constant was greatest for the tetra-substituted ammonium compounds, and for the solvent of lowest dielectric constant (chloroform) Attempts were made to apply additive rules proposed by Philip, Bouty and Silberstein with varying success More recently, Walden, Ulich and Werner[120] have found a lowering in ϵ at lower concentrations in such solutions of the salts of substituted ammonias with a subsequent rise with increasing concentration, so that curves showing minima often represent the results, as in the case of *tetrapropylammonium iodide* in *tetrachlorethane* This result is reminiscent of that of Furth[127] on aqueous solutions Krauss and Fuoss[170] have studied the influence of dielectric constant on conductance in the case of *tetra-substituted ammonium salts* in *ethylene dichloride*, *dioxan*, *benzene*, and mixtures of these It is found that specific influences due to the solvent are not conspicuously present In further work,[171] it was found that in *benzene* as solvent, the increase in dielectric constant due to dissolved substances was greater for electrolytes (*tetra-ammonium salts* and *silver perchlorate*) than for m-*dinitrobenzene*

According to the Debye theory, an applied electric field should result in the lowering of dielectric constant of a dipole solvent Although the evidence is somewhat conflicting, the conclusion appears to have been largely justified The lowering of dielectric constant in solutions containing ions may thus be associated with the polarization of the solvent by ions In more concentrated solutions, the degree of ionization may be less, and the effect of undissociated solute dipoles may enter in, causing an increase in dielectric constant as observed in many cases

The relation between the dielectric constants of solvents and their capacity to ionize has been the subject of extensive researches, particularly by Walden[172] Thomson[173] and Nernst[174] suggested many years ago that the dielectric constant of a solvent was the fundamental property determining its dissociating power Walden[175] investigated the electrical conductivities of substances in non-aqueous solvents, for example, in *liquid sulphur dioxide*, and found that many substances not normally regarded as electrolytes were capable of giving conducting solutions In the later work,[172] it was demonstrated, in the case of *tetraethylammonium iodide* in different solvents, that a close parallelism existed between dielectric constant and dissociating power of a solvent, the greater the dielectric constant of the solvent, the greater was the degree of dissociation of the salt of the substituted ammonium base for a given dilution The degree of ionization in a solvent was found to vary approximately as the cube of its dielectric constant In the course of this investigation, the related phenomenon of "electrostriction," whereby a decrease in volume occurs in connection with solution of a substance in a solvent having the power to produce a conducting solution containing ions, was also examined (No IX of the series of papers[172]) This effect had been previously observed by Drude and Nernst,[176] and by Kohlrausch and Hallwachs,[177] and was further investigated by Polowzow[178] for non-electrolytes It appears to be connected with the change of dielectric constant of a solvent with changing pressure, already noted

The case of *formamide* ($\epsilon = 84$) is of interest on account of the comparison afforded with water ($\epsilon = 79$) As solvents, the two liquids show great resemblance, and both cryoscopic and conductivity measurements have indicated that KI and $N(C_2H_5)_4I$ are about as highly ionized, other things being equal, in formamide as in water

Walden[179,180] also studied the effect of the dielectric constant of a solvent on the association of the solute It was found that the degree of association increased with decreasing dielectric constant

Schaefer and Schlundt[181] found certain cases of apparent exception to the Thomson-Nernst rule connecting ionizing power and dielectric constants of solvents It was found that the *liquid hydrogen halides* had low dielectric constants (ϵ_{HCl} = 4 6 at 27 7°C, ϵ_{HBr} and ϵ_{HI} being lower still), although they possessed marked ionizing power for organic acids and alcohols Palmer and Schlundt[182] further investigated the cases of *liquid ammonia, phosphine and stibine*, and found that liquid ammonia possessed the highest value (ϵ = 25 4) The decrease of dielectric constant with increasing molecular weight in the case of hydrides was thus confirmed Liquid ammonia, having a relatively high dielectric constant and good ionizing capacity, provided a case where the Thomson-Nernst rule held very well The authors added that, in view of the previous work on the hydrogen halides, such concord with the rule could not be safely predicted for liquid phosphine and stibine also

Two simple relations may be noted Sachanov and Pischeborowsky[183] studied the conductivities of solutions in solvents of low dielectric constant, and found that a law of the type λv^n = a constant held good, λ being the conductivity and v the dilution Walden[184] found the ionic conductivities at infinite dilution of solutions examined to vary inversely as the viscosities of the solvents

Four further researches remain for brief notice Williams and Allgeier[185] studied the influence on ϵ of changes of concentration of *benzoic acid, phenol, iodine, antimony trichloride, tin tetraiodide,* and *silver perchlorate* in *benzene* solution Haller and Ortloff[186] found decreased polarization in the case of solution of *acetylcellulose* in *aniline, methyl acetate, toluidine, methyl glycolacetate* and *methyl glycol* Wyman[187] has examined the dielectric constants of ampholytes forming zwitterions (*glycine, aminobutyric acid, glycine peptides*) in a variety of solvents (*ethyl alcohol, urea, glycine*), and finds that the dielectric constants of the solutions are practically additive properties of the constituents In certain cases, evidence of compound formation has been found in the behaviour of change of ϵ with concentration Thus maxima occur at 50% concentration for *phenol* dissolved in *quinoline*, and for *a-dinitrophenol* in *aniline*[278]

The work reported in the present and preceding sub-sections reveals a considerable number of curious discrepancies between the experimental results of different observers As noted previously, the results are sensitive to small temperature changes, and it may be that in some cases insufficient attention has been paid to thermostat control Further development in this field must await the advent of more consistent experimental evidence

(E) **Colloidal Solutions** In 1897, Drude[123] studied *gelatine gels* and found little variation in their dielectric constants compared with that of pure water Furth,[150] in an investigation already noted, showed that *gelatin* and *albumin solutions* gave dielectric constants whose values diminished with increasing concentration Walden[180] found that, for a given solute *tetraisoamylammonium iodide*, the tendency towards colloidal solution formation increased with decreasing dielectric constant of the solvent employed Thus *nitrobenzene* ($\epsilon = 35$) gave an ionized solution, *glacial acetic acid* ($\epsilon = 6$) and *chloroform* ($\epsilon = 5$) a molecular solution, and *benzene* ($\epsilon = 2\ 5$) a colloidal solution of the salt of the ammonium base Keller[152] determined the dielectric constants of a number of colloidal solutions by Drude's method, and found the results to be sometimes abnormally high and sometimes abnormally low Thus *fresh blood serum* gave a much higher value, whilst *hydrated colloids*, *gelatin* and *albumin* gave lower values, than water The dielectric constant of a *concentrated gold hydrosol* was found to be $\epsilon = 60$, and for a diluted sol, $\epsilon = 72$ Piekara[188] and Fricke,[189] however, report that the ϵ's of gold sols are about equal to that of water *Potassium hydroxide* in *toluidine* and *hydrogen chloride* in *benzaldehyde* were found by Keller to be molecularly dispersed and not ion-dispersed In the former case, the particles were electronegative, and in the latter, electropositive According to Werner's result that the ionizing capacity of a solvent varies directly as the cube of its dielectric constant, the ionization of a salt in water to that of the same salt in benzaldehyde would stand in the approximate ratio 80^3 15^3, or about 150 1

Marinesco[190] pointed out that it is possible to deduce the molecular weights of dissolved proteins by considering their dielectric constants as a function of wave-length It has been estimated by this method[160] that *gelatin* consists of molecules of different weights varying from 13,500 to 96,300

Further work on *seralbumin*,[191] *albumin*,[158,193,194] *casein gel*,[192] *gelatin*,[159,189,193] and various *serums*[193] may be noted Considerable divergence in dielectric behaviour is reported thus, whilst seralbumin has ϵ approximately equal to ϵ_{H_2O}, isoelectric sols of albumin and other proteins have high ϵ's, probably due to a preponderance of polar zwitterions In the case of seralbumin, it is necessary to suppose that the reactive amino and carbonyl groups are symmetrically distributed on the surfaces of the colloidal particles Casein gel shows increasing polarization with increasing water content, which may be ascribed to the formation of hollow spaces rich in water

The dielectric constants of sols containing rod-like particles showing double refraction have been investigated by Errera,[195] Szegvari[196] and theoretically by Bikerman [197] Frey[198] has also studied the double refraction of dispersoids in relation to the applicability of Wiener's mixture rule A noteworthy case is provided by ***vanadic pentoxide hydrosols***, the dielectric constants of which are abnormally high, being sometimes as great as 800, and decreasing with increasing dilution The dispersoid has high dipole moment,[199] causing orientation effects which vary regularly from place to place in the sol [*] Furth and Bluh,[200] using shorter wave-lengths than Errera, have shown that the dielectric constant of a freshly-prepared vanadic pentoxide sol is less, whilst that of a sol three years old is considerably greater, than that of water It appears that the effect of ageing in these sols is to produce the rod-like structure and to increase the dielectric constant Fricke[189] has advanced considerations against the rod-like particle theory, and holds that the important factor in increasing dielectric constants of sols is the entry of crystallization, which is responsible for the creation of new surfaces *Thorium hydroxide sols* have ϵ's much greater than that of water

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[*] The dipole moment is of the order $\mu = 415$ Debye units

The phenomenon of thixotropy, whereby sols set in certain circumstances into jelly-like masses, has also been considered from the standpoint of dielectric constant *Vanadic pentoxide sols* rendered thixotropic by sodium chloride,[202] and *stannic acids sols* treated with increasing amounts of hydrochloric acid causing setting,[189] have decreased dielectric constant The opposite appears to be true of *gelatin sols* [180] Thixotropy may be possibly accounted for by the formation of chains of water molecules, tending to link neighbouring colloidal particles together [201] On the rod theory, it would appear that in the thixotropic state the rods are partly held by these chains, so that they are not readily orientated by an applied field This would account for the observed decreased dielectric constants [202]

Errera[203] has studied the influence of ageing on the stabilities of HgS, CuS and Pt *alcosols*, in relation to their stabilities in dispersion media of varying dielectric constants Addition of substances having a higher dielectric constant than the solvent has no coagulating influence, whilst addition of bodies having a lower dielectric constant than the solvent causes coagulation, in increasing degree as the difference in dielectric constants increases

Millikan[204] tested the validity of Wiener's additive rule in the case of *emulsions of water* in a mixture of *carbon tetrachloride* and *benzene* It was found that by making an approximation owing to the relatively high value of the dielectric constant of water, the relation held to within 1% of the observed values

Piekara[205] has found that the dielectric constants of fine particle emulsions are not in good agreement with the requirements of an extended Clausius-Mosotti formula The importance of sizes of particles and the extent and nature of their surfaces is emphasized It is suggested that the changes of dielectric constants with particle size may be connected with adsorption at surfaces, the field at the exterior of particles being different from that in the interior

Further work includes measurements of the ϵ's of colloidal solutions of *diamine blue, diamine black* and *methylene blue,*[206] of *acetylcellulose* in *methylglycol acetate, methyl glycol, diacetone alcohol, ethylacetoglycollate,*[186] and of *polyindenes* and *polystyroles*[207] In the cases of the last-named types of high molecular weight, the polarizations show maxima in the more highly-dispersed colloidal region, whilst the dipole moment increases with increasing molecular weight

Two papers relating to the orientation of colloidal particles in an alternating field are worthy of notice By the method of calculating molecular weights from data of change of ϵ with frequency, it is found possible to distinguish between mono-disperse (equal-sized particle) and poly-disperse (different-sized particle) systems[208] A new expression is developed for relaxion time,[209] and it is shown that the behaviour, predicted by Wagner, for an assemblage of spheres having different conductivities may result in a poly-disperse system The importance of particle size and distribution in size becomes clear

(F) **Liquid Crystals.** Lehmann[210] characterized liquid crystals as substances of high molecular weight intermediate in nature between truly amorphous liquids and crystalline solids Bose[211] interpreted the phenomenon by a tendency, associated with double refraction, to parallel orientation on the part of the molecules concerned Ježewski[212] and Kast[213] investigated the connection between dielectric constant of liquid crystals and their orientation in a magnetic field (see this vol 15D) Kast found that this group of substances might be divided into two classes, according as the long axes of the molecules were the directions of least or greatest dielectric constant Ornstein[214] obtained results in general agreement with those of Kast The two classes named correspond to symmetrical and unsymmetrical molecules respectively; for the former class, ϵ decreases, and for the latter, ϵ increases with increasing magnetic field, when the substances are examined in the melted condition[215]

The X-ray photographs of liquid crystals in an alternating field, as well as measurements of dielectric losses, prove the existence of a critical frequency at which anomalous dispersion sets in (see section 27Ac above) [216] This critical frequency is sensitive to changes in temperature[216] and to the presence of impurities [217] The dielectric losses in p-*azoxyanisole* give a large temperature gradient, involving difficulties with Debye's frictional theory of anomalous dispersion [218]

The swarm theory of liquid crystals (see this vol 15D), as developed by Kast and Ornstein, involves groups each containing perhaps 10^5 molecules [215,216] The molecules within any given swarm lie parallel, but the swarms themselves are normally distributed at random, so that the whole is anisotropic The complete alignment of the swarms with an applied alternating electric field occurs at the critical frequency mentioned above The rotation moments are large, and about 10^5 times the molecular moment [215,216] Dielectric measurements in p-*azoxyanisole* and *benzophenone* show that immediately prior to fusion the swarms are in a state of quickly-changing dimensions [219] Further information is available in the literature cited

28. The Dielectric Constants of Solids

(A) **Experimental Data.** (a) *Inorganic Substances* The more recent results on the dielectric constants of solids include measurements on the following — *Ice*[227,220,236], *Oxides* (MO type) of Mg,[224,237] Cu,[232] Sn,[237] Hg,[237] Pb,[237] (M_2O_3 type) of Al,[224] Cr,[224] Sb,[224] Bi,[224] (MO_2 type) of Ti,[228,220,237] Zr,[224,237] Ba,[224] Ce,[224] Th,[224] (other types) Ag_2O,[232] Sb_2O_4,[224], Ta_2O_5,[224,237] WO_3,[237] U_3O_8,[237] *Fluorides* of Li,[222,220] Na,[222,229] K,[229] Rb,[220] Mg,[228,229] Ca,[228,229] Sr,[228,229] Ba,[228,229] Fe,[229] Co,[229] Ni,[229] *Chlorides* of Li,[225,229] Na,[222,225,229,232] K,[222,225,229,232,237] Rb,[222,225,229,232] Cs,[225,232] Tl,[222,237] Sr,[237] Pb,[237] *Bromides* of Li,[223,220] Na,[222,223,220] K,[222,220] Rb,[222,220,232] Cs,[232] Tl,[222] *Iodides* of Li,[223,220] Na,[223,229] K,[222,229] Rb,[222,229,232] Cs,[232] *Carbonates* of Li,[225] Na,[225] K,[225] Rb,[225] Cs,[225] Be,[225] Mg,[225,231] Ca,[225,231] Si,[225] Ba,[225,231] Mn,[231] Zn,[231] Pb,[231] *Nitrates* of Na,[225] K,[225] Ca,[225,220,231] Sr,[225,229,231] Ba,[225,229,231] Pb,[229,231] *Sulphates* of Sr,[231] Ba,[231] Pb;[231] *Cupric sulphate pentahydrate*,[229,231] *Sodium thiosulphate pentahydrate*,[229,231] *Normal and acid phosphates* of Na,[237] K,[228,237] *Dihydrogen arsenates* of Na,[237] K ,[223,237] *Arsenites* of Na,[237] K ,[237] the *sulphide,*[237] *chlorate,*[223] *bromate,*[223] *iodate,*[223] *cyanide*[223] and *thiocyanate*[223] of *potassium* , *Platinocyanides* of Mg,[231,238] Ca,[231] Sr,[231] Ba,[231] Yt ,[238] *Rochelle salt* ,[221,229,233,234,236] *Calcium tungstate* ,[237] *The alums* ,[230] *Hydrocyanic*[220] and *Silicic*[243] *acids* , *Glass*[226,240] and *Porcelain* [240]

(b) *Organic Substances Methyl chloride* ,[239] *Methylene chloride* ,[239] *Methyl bromide* ,[239] *Methyl iodide* ,[239] *Carbon tetrachloride* ,[239] *Benzene* ,[239] *Bakelite,*[240] *Keramot,*[240] *Ebonite,*[240] *Paxolin,*[240] *Millboard,*[240] *Rubber,*[240,242] *Chlorinated diphenyls,*[241] *Sugar,*[243] *Starch,*[243] *Brown charcoal,*[243] *Tobacco,*[243] *Cellophane*[244] and *Cellulose acetate* [244]

(B) **Influence of Conditions** The dielectric constant of a solid is less for the powdered than for the compact state Results obtained by Baumann are recorded by Heydweiller [245]

The influence of temperature was studied by Joachim,[246] who obtained constant ϵ's between 17° and −180°C for powdered *sulphur, ammonium sulphate, mercuric chloride* and *cyanide,* and *lead chloride* Dieterich[247] found, however, that the available data on solids indicated a small positive temperature coefficient Further measurements on *fluorspar, gypsum* and *glass* yielded temperature coefficients of 2 05, 3 75 and $1\ 37 \times 10^{-4}$ respectively, whilst the value for *quartz* was very small indeed Bretscher[248] has discussed the temperature variation in the case of ionic crystals , the predictions of theory are not fulfilled in the cases of *sodium chloride* and *calcium fluoride* This may be in part attributed to the incorrectness of the Born type of potential function (see Vol 1 19A)

In general, a discontinuous change in ϵ occurs when a substance passes from the liquid to the solid state (see Vol 1 15) [76] Errera[229] has concluded that liquids containing non-polar molecules, for example, *benzene, hexane,* p-*dichlorobenzene* and *titanic chloride,* have increased ϵ on solidification, whilst the reverse occurs for frequencies at which the dipoles continue to oscillate in the case of polar liquids, for example, *water, nitromethane, methyl cyanide* and *nitrobenzene* The dielectric constant of *phosphorus pentachloride* rises on solidification [249] In the cases of *hydrogen chloride,*[62,250] *bromide*[250] and *iodide,*[250] for some distance below the melting point, the solid molecules appear to orientate themselves in an applied field to about the same extent as in the corresponding liquid states, after which ε drops suddenly within 0.1°C. The transition temperatures between different modifications are clearly shown by breaks in the ε curves. It has been shown in the laboratory of Kamerlingh-Onnes[4] that in the case of solid *hydrogen* a maximum ε is reached at the melting point, as in Table XXXV.

TABLE XXXV.—DIELECTRIC CONSTANTS OF LIQUID AND SOLID HYDROGEN

Liquid Hydrogen			*Solid Hydrogen*		
Pressure (mm Hg)	Temperature (°K)	ε	Pressure (mm Hg)	Temperature (°K)	ε
755	20.33	1.225	58	14.0	1.248
357	18.05	1.234	42	13.5	1.224
80	14.61	1.211	35	13.3	1.212
			32	13.2	1.211

An interesting case is provided by solids having highly viscous liquids. For example, *glucose*[251] shows no discontinuity in ε on passing from viscous liquid to solid state. Similar results are recorded for *borate glasses*.

Evidence of compound formation may sometimes be gained from a study of the variation of ε with composition: thus Lowry and Jessop[252] found a pronounced maximum at the composition corresponding to SCl_4 in the case of solid *sulphur-chlorine* systems. *Glasses*[226] show increasing ε with increasing metallic oxide content relatively to silica. *Rubber*[242] is found to give a maximum ε for 11.5% sulphur, falling to a minimum at 22%S, and rising again up to 32%S. In the *alums,*[230] ε appears to be a measure of the force by which H_2O is held by the solid. thus it is greatest when the atomic volume of the replaceable metal is least.

Gudden and Pohl[253] found that light falling upon phosphorescent *Sidot blende* (zinc sulphide containing a minute trace of copper) was accompanied by an increase in dielectric constant. This effect is apparently connected with the displacement of electrons from copper to sulphur under the influence of light, the return of these electrons being responsible for the phosphorescent properties of the substance, in accordance with Lenard's view. It may be supposed that the shifting of electrons increases the polarization of the substance and thereby the dielectric constant is also increased. The effect was further investigated by Molthan,[254] who found that with decreasing wave-lengths the raising of ϵ by light was diminished. Wilde[255] found that the effect reached a maximum at about 140°C. Herweg[256] further studied the temperature influence, and the effect of varying electric fields.

A few further results may be noted. Guében[257] showed that irradiation of thin layers of solid dielectrics with rays from radium bromide appeared to produce no change in ϵ, to within 1 part in 1,000. Layers of *aluminium oxide*, *antimony tetroxide*, *bismuth trioxide*, and *zirconium oxide*[258] have ϵ independent of field intensity up to 12 × 10 volts per cm. *Ebonite*, *vulcanite* and *glass*[259] show strongly-marked maxima in the wave-length region 200 to 1,000 metres. The dielectric losses and power factor of *sodium chloride*[260] have been studied. The presence of moisture is found to increase the power factor.

(C) **Additivity Rules.** Heydweiller[245] attempted to apply Wiener's formula (this vol. 27B), putting $u = 4$, to salt hydrates where the dielectric constants were known for the anhydrous and hydrated salts, and thus to determine the ϵ of water in such cases. It was also found that Pd/M was approximately twice Rd/M (see equations (4) and (6) of this chapter) for many salts examined. Molecular refraction corresponds to electron polarization, whose absorption region is in the visible and ultra-violet, whilst molecular polarization corresponds to atom polarization in the infra-red. It thus appeared that electron and atom polarization were about the same in these cases

John[261] studied the applicability of Wiener's rule to mixtures of *air* and *solid bodies* of known shape, for example, brass spheres or rubber cubes Stoecker[262] carried out a similar investigation on mixtures of *potassium chloride* and *air*

Tausz and Rumm[243] studied ϵ's of hydrated materials, and found a logarithmic mixture rule for the solid and air to be applicable The ϵ's increase with increasing water content, and show increasing variability with temperature, as illustrated, for example, by dried and hydrated *silicic acid* Further, for the same water content, different specimens of *starch* gave different ϵ's This was attributed to varying proportions of " movable " water, having high ϵ, and " fixed " water, having lower ϵ

(D) **Nature of Dielectric Polarization in Solids.** Lydia Inge and Walther[263] placed a crystal of *sodium chloride* between a point and a plane electrode under oil, and subjected it to " surge " potential of short duration It was found that the discharges took place along certain preferred directions, running from the point in the surface in the directions of the four diagonals of the crystal cube

Murphy and Lowry[264] hold that in solid dielectrics direct current conduction takes place along a system of channels of sub-microscopic size (compare Smekal's theory of crystals in Vol 1 21C) Dielectric loss, associated with electrical energy converted into heat, takes place on account of free ions, adsorbed ions or polarization of molecules, and the authors discuss the possible mechanism of the process Williams[265] has considered the channel conduction theory in relation to the micelles existing in *cellulose, silk* and *tissue* (this vol 17), and concludes that conduction is due to ionic processes operating between fibres and chains Similar views are expressed by Stoops [244] X-rays[266,267,268,269] have been applied to the problem, with the general conclusion that the passage of electricity through solid dielectrics must be associated with conduction by ions Experiments have been undertaken in this connection on *ceresine* and *paraffin wax*

Errera and co-workers have carried out a large amount of work on the dielectric properties of the solid state, with special reference to polar crystals A summary of the position is due to Errera[239] Errera and Sack[238] divide solid dielectrics into three classes typically polar lattices, molecular lattices, and polar lattices having dipole moment In the last-named case, exemplified by *ice* and *Rochelle salt*, the dipoles are apparently free to rotate in the solid state Errera's work is further considered in this Vol 34A A bibliography of work on ϵ's, dielectric losses and allied subjects from 1931 to 1934 may be noted[270]

The results recorded in the present chapter consist of an array of experimental facts which appear largely unco-ordinated It soon becomes clear that dielectric constants are less important theoretically than the corresponding molecular polarizations (derived by equation (4)) Moreover, molecular polarization itself, in general, is complex, and may consist of three parts, termed electron, atom and orientation polarizations, each superimposed upon the others The distribution between the separate parts may be more important than the total polarization It need not appear very surprising, therefore, if no clear relations are found between dielectric constant and molecular constitution Regularities appear when the parts are treated separately These and kindred matters form the subject of the chapters immediately following

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(A list of abbreviations used in references will be found on pages xxxi et seq)

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CHAPTER XI

THE DEBYE THEORY OF POLARIZATION

29. The Clausius-Mosotti Function

In ordinary circumstances, unpolarized matter may be regarded as electrically homogeneous. Polarization involves the introduction of inhomogeneity into a system, such as the displacement of positive and negative charges relative to each other.

The Clausius-Mosotti polarization formula is here deduced by the "cavity" method,[1,2] according to the classical theory, prior to the work of Debye.

Let us consider a dielectric medium to which an external field may be applied (Figure LXV). The field corresponds to a positive charge on a plate A, and a negative charge on plate B, the field direction being from A to B. Polarization by induction causes the molecules of the dielectric to form into chains as diagrammatically represented. According to the classical procedure, two cases are considered :—

(a) A long cylindrical cavity is chosen in the medium, assumed to be of infinite length and infinitely small cross-section. This is represented by C in Figure LXV. The choice of this cavity is such that no molecules of the medium are included in it, and the field acting in it is that which would operate if the effect of the medium were eliminated. The force on a unit charge within this cavity is represented by E, which is the same as the intensity of the internal field in the case where matter is absent, the internal field being equal to the applied external field.

(b) An infinitely narrow section D of unlimited area of cross-section is chosen, again in such a way that no molecules are included between the imaginary plates delimiting the section, The field, or force on unit charge, between the plates is now not equal to E, for the induced charges on the plates must be taken into account. This field is represented by D, sometimes called the " electric displacement."

Let n be the number of molecules per unit volume of the medium, and let P_n be the polarization or induced electric moment of unit volume. Then the field in case (b) above due to the surface charges on the plates is given, according to Gauss' theorem, by $4\pi P_n$, so that

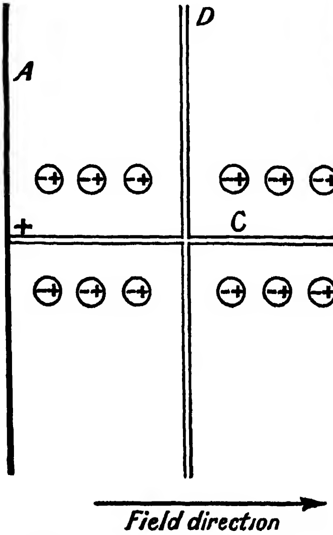


FIGURE LXV —EFFECT OF EXTERNAL FIELD ON A DIELECTRIC MEDIUM.

$$D = E + 4\pi P_n \quad \dots\dots\dots\dots \quad (1)$$

Moreover, the ratio D/E is that of the field in the cavity D of Figure LXV with the medium present to the field with the medium removed. This ratio, according to Maxwell, is equal to the dielectric constant ϵ, so that

$$D = \epsilon E \quad \dots\dots\dots\dots \quad (2)$$

This result may be compared with the equation $B = \mu H$ in the corresponding magnetic case (see Vol. 1: 24B).

Now owing to the mutual interaction of the molecules of the medium, the field acting on a molecule is greater than E, and may be represented by F. Then, with certain assumptions, in accordance with the classical theory,[3]

$$F = E + \frac{4\pi P_n}{3} \quad \dots\dots \quad (3)$$

The field F is responsible for setting up the induced molecular moment m. The polarizability α being defined as the moment induced by unit field, it follows that

$$m = \alpha F \quad \dots\dots \quad (4)$$

Also, by the definition of P_n,

$$P_n = m \cdot n \quad \dots\dots \quad (5)$$

From (1) and (2), eliminating D,

$$P_n = \frac{E(\epsilon - 1)}{4\pi} \quad \dots\dots \quad (6)$$

Also from (4) and (5),

$$P_n = \alpha F n,$$

whence, using (3),

$$P_n = n\alpha(E + \frac{4}{3}\pi P_n),$$

which leads to

$$P_n = \frac{n\alpha E}{1 - \frac{4}{3}\pi n\alpha} \quad \dots\dots \quad (7)$$

Thus, equating the values of P_n given by (6) and (7),

$$\frac{\epsilon - 1}{4\pi} = \frac{n\alpha}{1 - \frac{4}{3}\pi n\alpha},$$

whence

$$\frac{\epsilon - 1}{3} = \frac{\frac{4}{3}\pi n\alpha}{1 - \frac{4}{3}\pi n\alpha}$$

and

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi n\alpha \quad \dots\dots \quad (8)$$

so that the function on the left-hand side of (8) is equated to a term which involves constants depending on the dielectric only, and should be independent of temperature. This expression involves n, the number of molecules in 1c.c., which is directly proportional to the density of the dielectric medium. Multiplying both sides of (8) by the molecular volume $V = M/d = N/n$, where M is the molecular weight of the dielectric, d the density, and N is Avogadro's number, the following expression is reached for the molecular polarization P (compare equation (4) of Chapter X):

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4}{3} \pi N \alpha = 2{\cdot}54 \times 10^{24} \alpha \quad \ldots\ldots \quad (9)$$

This is the Clausius-Mosotti relationship, fundamental to the present discussion. Perhaps the only seriously doubtful part of the argument lies in the derivation of equation (3), here omitted, and in the true interpretation of F. According to Keyes and Kirkwood,[4] the Clausius-Mosotti function is not quite independent of density, and, whilst furnishing a good and useful approximation, is not in exact agreement with the facts except in the limiting case of infinitely low density. An amended formula is proposed.

In the case of gases, ϵ does not differ greatly from $\epsilon = 1$. Here the denominator of the function $(\epsilon - 1)/(\epsilon + 2)$ may be written as equal to 3, giving, according to equation (9),

$$3P = (\epsilon - 1) \cdot \frac{M}{d} = 4 \pi N \alpha \quad \ldots\ldots\ldots\ldots\ldots \quad (10)$$

Further, in the general case, the electric moment for unit field F is given, according to (4) and (5), by the expression

$$P_{n_1} = n\alpha = \frac{3}{4\pi} \cdot \frac{\epsilon - 1}{\epsilon + 2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

If the induced moment m corresponds to the separation of charges e by a distance equal to s,

$$m = s \cdot e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

In the case of infinitely long waves (static fields), the molecular polarization may be represented by P_0. Here, within the limits of Maxwell's relation $\epsilon = r_\infty^2$, the molecular refraction R may be written

$$R = \frac{r^2 - 1}{r^2 + 2} \cdot \frac{M}{d} = \frac{4}{3}\pi N a \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

where r is the index of refraction for infinitely long waves. It often happens that Maxwell's relation does not hold, however. This case is discussed below.

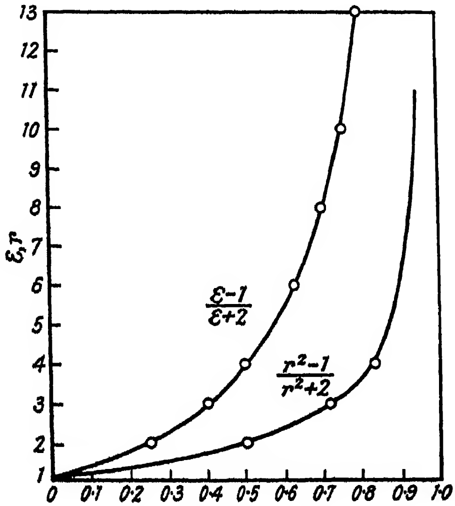


FIGURE LXVI.—CURVES SHOWING VARIATION OF SPECIFIC POLARIZATION WITH DIELECTRIC CONSTANT, AND OF SPECIFIC REFRACTION WITH INDEX OF REFRACTION. Both curves become asymptotic to the line on the extreme right of the Figure as the dielectric constant and index of refraction respectively approach infinity.

The function $(\epsilon - 1)/(\epsilon + 2)$ may be termed the specific polarization Π, and it is of interest to note in what way this and the corresponding specific refraction vary with ϵ and r respectively. The curves are shown in Figure LXVI. It is seen that for small values of ϵ, Π changes rapidly with changes of ϵ; for values of ϵ between 10 and ∞, Π varies from 0·75 to 1, the curve becoming asymptotic to the $\Pi = 1$ line. Here changes in ϵ produce little effect upon Π. It is nevertheless true that Π always increases as ϵ increases. In the specific refraction curve, the same considerations hold, but the effects are more pronounced, the function changing more rapidly for lower values, and more slowly than in the case of the dielectric constant curve for higher values of r.

It may also be noted that the quantities designated by P_n and P in the above argument are different in nature and have different dimensions. P_n varies with the external field (equation (6)), whilst P should be independent of field (equation (9)). Moreover, P has the dimensions of M/d, that is, of volume; whilst P_n has the dimensions of electric moment (or charge times length) per unit volume (equation (5)). The relation between the two quantities is given, according to (4), (5) and (9) by

$$\frac{P_n}{P} = \frac{3}{4\pi} \cdot \frac{d}{M} \cdot F \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

It is observed that combination of (9) and (14) for the case $F = 1$ leads to the value of P_{n_1} given in equation (11).

W. L. Bragg[5] summarizes the effect of radiation in polarizing matter in the following way: "According to the electromagnetic theory of light, the retardation of light passing into a medium from space is due to the electric polarization of the atoms of the medium under the influence of the light wave. The greater the total electrical moment per unit volume produced by the wave, the slower it travels, and the higher is its refractive index."

30. The Evidence for Permanent Molecular Moment

The considerations advanced in the preceding section refer to the case of molecular moment induced by an external field. It is now necessary to examine three lines of evidence for the existence of "polar molecules," having intrinsic or permanent electric moment, related in some way to their normal structure in the absence of an applied external field.

(A) **Polarization and Refractivity.** So long as the Maxwell relation $\epsilon = r_{\infty}^2$ is fulfilled, then P given by (9) is equal to

R given by (13), and it is then possible to calculate values of the polarizabilities α of atoms, ions and groups from measurements of the refractive indices r of different substances. This arises from the fact that in such cases molecular refraction R is found to be an additive and constitutive property, so that definite refraction allotments can be made to the individual atoms or atomic groups constituting a molecule. Heydweiller[6] made measurements of the refractive indices of solutions, and Spangenberg[7] of solid salts of the alkali halide series. These results were utilized by Fajans and Joos[8] and by Born and Heisenberg[9] to calculate the refractions and polarizabilities of inert gas-like ions. Debye gave the following Table XXXVI of ionic refractions (see the book: *Polar Molecules*).

The measurements of Wasastjerna were made on solutions, whilst the refractivities of Fajans and Joos are for the free gas ions.

TABLE XXXVI.—REFRACTIVITIES OF INERT GASES AND RELATED IONS.

W Wasastjerna FJ Fajans and Joos

	W		W	FJ		W	FJ		W	FJ		W	FJ
O^{--}	4·06	F^-	2·20	2·44	Ne	1·01	1·00	Na^+	0·74	0·50	Mg^{++}	0·44	
S^{--}	15·0	Cl^-	8·45	9·00	A	4·23	4·20	K^+	2·85	2·23	Ca^{++}	1·99	
		Br^-	11·81	12·67	Kr	6·42	6·37	Rb^+	4·41	3·58	Sr^{++}	3·22	
		I^-	18·17	19·24	Xe	10·56	10·42	Cs^+	7·36	6·24	Ba^{++}	5·24	4·28

From these refractivities, the polarizabilities of the ions may be calculated using (13), by which $\alpha = 3R/4\pi N$, or $0{\cdot}394 \times 10^{-24}R$, inserting the values $N = 6{\cdot}06 \times 10^{23}$ and $\pi = 3{\cdot}14$. This gives, for example, the polarizability of the fluorine ion F^- as $0{\cdot}87 \times 10^{-24}$ (see Table XXXVII). Born and Heisenberg[9] evaluated the polarizabilities of Li^+, Na^+ and K^+ as $0{\cdot}075$, $0{\cdot}21$ and $0{\cdot}87 \times 10^{-24}$ from the theory of spectra, in connection with the effect of the deformabilities of ions on the Rydberg constant. From these numbers, other values were obtained by difference from Spangenberg's measurements. The deformabilities of the inert gases were calculated by means of the Lorenz-Lorentz formula, using the indices of refraction taken from tables and extrapolated to infinite wave-length. Mayer[10] calculated the polarizabilities of ions of rare gas type by the method of Born and Heisenberg, using corrections for penetration and higher order deformation of ions, with the result that the values for positive ions were found to be lower, and for negative ions higher, than had been previously assumed. Schoppe,[11] following the method of Herzfeld and Wolf,[12] obtained results in essential agreement with those of Mayer in the case of univalent positive ions. The results are collected in Table XXXVII.

TABLE XXXVII.—POLARIZABILITIES OF INERT GASES AND RELATED IONS. ($\times 10^{24}$)

W Wasastjerna. BH Born and Heisenberg M Mayer S Schoppe

	W		W	BH	M		W	BH		W	BH	M	S		W	BH
						He		0 20	Li^+		0 075	0 030	0 024			
O^{--}	1 60	F^-	0 87	0 99	0 90	Ne	0·25	0 39	Na^+	0·18	0·21	0·182	0 15	Mg^{++}	0 11	0 12
S^{--}	5 81	Cl^-	3 33	3 05	2 95	A	1 05	1 63	K^+	0 71	0·87	0 844	0 74	Ca^{++}	0 49	
		Br^-	4 67	4 17	4 06	Kr	1·60	2 40	Rb^+	1 10	1 81	1·42	1·38	Sr^{++}	0 80	1 42
		I^-	7 28	6 28	6 00	Xe	2 63	4 00	Cs^+	1 82	2·79	2 45	2 38	Ba^{++}	1·30	

Al^{+++} (BH) 0 065 Si^{++++} (BH) 0 043

Born and Heisenberg used their values of $\bar{\alpha}$ in connection with (i) effective nuclear charges of inert gas-like ions, and (ii) the vaporization heats of the alkali halide salts. With regard to (i), a relation of the type $\alpha = C(Z - s_p)^{-3}$ was found to fit the facts, C and s_p being constants for a given set of ions having the same number of outer electrons, for example, in the series F^-, Ne, Na^+, Mg^{++}, Al^{+++}, Si^{++++}. The quantity $Z - s_p$ measured the effective nuclear charge, the shielding constant s_p due to the outer electrons being taken as O for the He("K"), 6 for the Ne(" L "), 13 for the A(" M "), 28 for the Kr(" N ") and 46 for the X(" O ") series. When $\log(Z - s_p)$ was plotted against $\log \alpha$ on a graph diagram, linear relationships were found for each set of ions, as shown in Figure LXVII. The question raised under (ii) above is mentioned in relation to the boiling points of the alkali halides (see Section 9A). Born and Heisenberg considered the energy necessary for building up the vapour molecule from the free ions. This equals $-V$, where V, the heat of formation of one gram-molecule of vapour from the free gas ions, is a function of the deformabilities of the ions. The value of $-V$ is given by the sum of a number of terms, representing (a) the potential energy of the two ions (negative attractive term $-e^2/r$ and positive repulsive term be^2/r^9); (b) the energy of setting up dipoles in the ions ($m_1^2/2a_1$ plus $m_2^2/2a_2$, where m_1, m_2 are the induced dipole moments, and a_1, a_2 are the polarizabilities of the ions); (c) the attraction between the charges of the ions and the induced dipoles

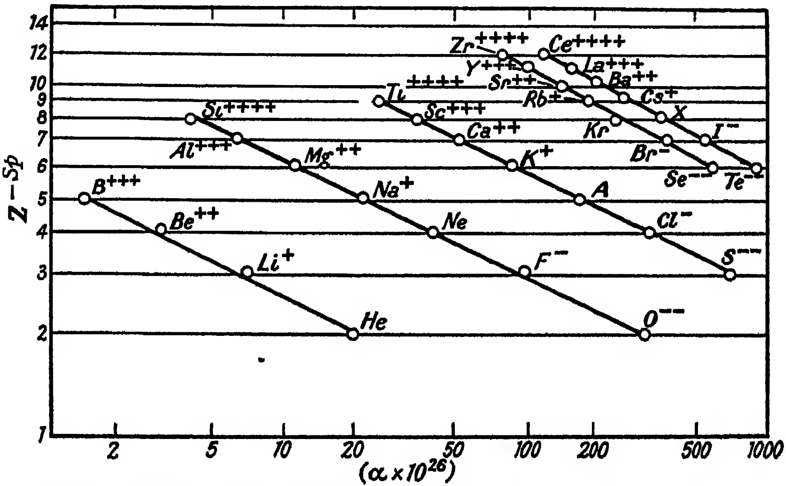


FIGURE LXVII.—RELATIONSHIP BETWEEN THE LOGARITHM OF EFFECTIVE NUCLEAR CHARGE OF IONS OF THE SAME TYPE AND THE LOGARITHM OF POLARIZABILITY. Ions of the same type have the same number of extranuclear electrons, as in the series Na^+, Ne (inert gas), F^- and O^{--}.

(negative terms $-em_1/r^2$, em_2/r^2); (d) the term representing the interaction of the dipoles (negative, equal to $-2m_1m_2/r^3$). For the derivation of these terms, see the appendix to Chapter XIV, where it is shown that the potential energy of a dipole is $-m^2/2a$, so that the work done in setting up a dipole is the same quantity with sign reversed. Manipulation of the summation of these terms then leads to an expression for V in terms of a_1 and a_2 and other constants, so that V can be calculated.

The lattice energies of the alkali halides U had also been found, in connection with Born's lattice theory. Now, according to the theory outlined in Vol. I . 13, the energy difference $U - V$ should be equal to the sublimation heat S. The values of $U - V$ are compared with von Wartenberg's experimental values for the vaporization heat values for Q (see Vol. I : Table XIX). The agreement is seen to be generally good (Table XXXVIII). The widest divergences occur for the cæsium salts.

TABLE XXXVIII.—DERIVATION OF HEATS OF SUBLIMATION FROM POLARIZABILITIES.

Born and Heisenberg used von Wartenberg's values of Q, the heats of volatilization and not his estimates of S, the heats of sublimation

	U	V	U-V	S (Q)		U	V	U-V	S (Q)		U	V	U-V	S (Q)		U	V	U-V	S (Q)
NaF	222	161	61	56·6	KF	191	140	51	41·9	RbF	163	122	41	40·0	CsF	170	129	41	31·7
NaCl	182	139	43	44·3	KCl	164	124	40	40·5	RbCl	156	119	37	37·8	CsCl	146	115	31	37·4
NaBr	172	133	39	38·6	KBr	156	120	36	38·2	RbBr	149	115	34	37·0	CsBr	139	110	29	40·7
NaI	158	126	32	37·0	KI	145	113	32	37·2	RbI	140	110	30	37·0	CsI	131	105	26	40·0

The above considerations apply to the inert gas-like ions, for which the rule of additivity of molecular refraction holds particularly well; in other cases, the Maxwell relation $\epsilon = r^2$ breaks down, and the additivity rule also. In illustration, oxygen and ammonia gases may be compared. Thus, for oxygen at N.T.P., $\epsilon - 1 = 0{\cdot}000543$, and $r_\infty^2 - 1$ approximately $= 0{\cdot}00053$, showing that the rule is applicable. For ammonia under the same conditions, $\epsilon - 1 = 0{\cdot}0084$, whilst $r_\infty^2 - 1 = 0{\cdot}00074$. The additivity rule for molecular refraction also breaks down for ammonia; thus, $R_{NH_3} = 6{\cdot}3$ c.c., $R_N = 2{\cdot}16$ and $R_H = 1{\cdot}02$, so that R_{NH_3} according to the additivity rule should be $R_N + 3R_H$, or $2{\cdot}16 + (3 \times 1{\cdot}02) = 5{\cdot}22$. Similar results are found in the case of the hydrogen halides,[13] for which "apparent polarizabilities" of the negative ions (α' and α'') have been calculated (this vol.: 42A). Such anomalous molecular refraction for ammonia, the hydrogen halides, and other cases requires special explanation, which is found by considering these molecules as possessing permanent electric moment. This line of argument provides the first link in the evidence for the existence of polar molecules.

(B) **Polarization and True Molecular Volume.** It has been observed that molecular polarization P and polarizability α, in agreement with equation (9), have dimensions of volume. According to the earlier interpretation of polarizability, if a molecule is treated as a conductive sphere of radius r in a field whose intensity is F, then it assumes a moment m induced by the field given by

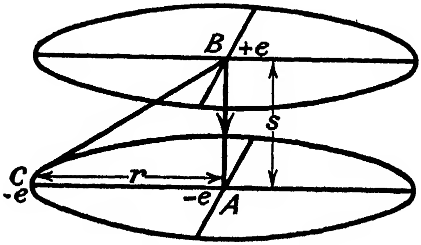


FIGURE LXVIII.—Shift of a Bohr Circular Orbit under a Field at Right Angles to its Plane.

$$m = r^3 F \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

Comparing (4) and (15), $\alpha = r^3$, so that the molecular polarization P is measured by $\frac{4}{3}\pi r^3 N$, which is equal to the true volume of the molecules in one gram-molecule of substance, since $\frac{4}{3}\pi r^3$ is the volume of a sphere of radius r.

A proof of the relation (15) in the particular case of the shift of a Bohr hydrogen circular orbit by a field acting at right angles to the plane of the orbit is usually given somewhat as follows. In Figure LXVIII, let the field F act in the direction AB, causing a shift in the position of the orbit through a distance s in the direction marked by the arrow, the nucleus remaining at B, and the electron circulating in the orbit whose centre is at A. The effect is to set up a dipole having charges

$+e$, $-e$ at B and A respectively, with resultant dipole moment m given by

$$m = e.s = a.F \quad \text{(16)}$$

The circulating electron, however, is never at A, but occupies positions such as C. The force due to the field, namely $e.F$, may then be equated to the resolved part of the Coulomb field acting in the opposite direction between A and B. This is given by $\frac{e^2}{BC^2}\cos\hat{CBA}$ or $\frac{e^2.AB}{BC^3}$. But the shift AB $= s$ will be small compared with the radius of the orbit AC, so that BC may be put equal to AC with sufficient approximation, whence

TABLE XXXIX.—RELATION BETWEEN TRUE MOLECULAR VOLUMES AND POLARIZABILITIES.

Molecules of Class I			*Molecules of Class II*		
Molecule	$b/4$	P	Molecule	$b/4$	P
H_2	4·1	2·0	NH_3	8·8	57
A	8·0	4·2	C_2H_5Cl	22·0	116
C_2H_4	14·0	9·4	H_2S	7·9	30
C_5H_{12}	36·0	26·0			

$$e.F = \frac{e^2.AB}{AC^3}$$

which gives

$$F.AC^3 = e.s \quad \text{(17)}$$

Comparing (16) and (17), $a = AC^3$, the cube of the radius of the orbit. Hence, putting AC $= r$, equation (15) follows at once.

Assuming then that molecular polarization should be a measure of true molecular volume, it is possible to compare P with estimates of the volumes of molecules in a gram-molecule of substance (calculated from $b/4$, where b is the second constant occurring in van der Waals' gas equation). It is then found that in certain cases the agreement lies within the experimental error, whilst in others there is complete disagreement, as shown in Table XXXIX.

The figures of Table XXXIX provide a second argument in favour of the existence of two kinds of molecule. It is suggested in Debye's theory that the molecules of Class II are characterized by permanent electric moment. Ammonia again falls into the group showing abnormality.

(C) **Polarization and Temperature.** According to the theory outlined in Section 29 above, molecular polarization should be independent of temperature change. In Chapter X, various results are recorded in complete disagreement with this view. In cases where discrepancies occur, however, it is found that, in general, a relation of the type of equation (8) of Chapter X accounts for the facts very well.

Debye[2,14] introduced the theory of molecules possessing permanent electric moment as an explanation of this difficulty and of those noticed above. Certain molecules, such as NH_3 and H_2O, have an irregular distribution of positive and negative charges in such a way that the centres of gravity of the opposite charges do not coincide, this being an intrinsic property of such molecules and independent of external fields. The separation between the positive and negative centres is the "dipole distance" d, so that the intrinsic moment μ is equal to the product of the electronic charge with d. Debye considers the effect of an external field upon a gaseous system containing such polar molecules. The tendency will be for the molecules to orientate themselves along the field direction, but this is resisted by their thermal agitation which is more pronounced at high temperatures. When the field is produced between condenser plates, only those molecules which are sufficiently near to the electrodes will be completely orientated (Figure LXIX); similar considerations apply to the field in the neighbourhood of a gas ion. Treating the molecules as rigid systems of charges, by a statistical argument, it is found that an effective dipole moment equal to $\mu^2F/3kT$ is set up in the field direction, as in the magnetic case (equation (9) of Vol. 1: 27A). The molecules are not, however, generally rigid, and thus the polarization term associated with α must be added to the term connected with permanent electric moment. This yields the following expression for molecular polarization :

$$P = \frac{\epsilon - 1}{\epsilon + 2}\cdot\frac{M}{d} = \frac{4}{3}\pi N\left(\alpha + \frac{\mu^2}{3kT}\right) \ldots\ldots\ldots\ldots \quad (18)$$

where k is Boltzmann's constant ($1{\cdot}37 \times 10^{-16}$ erg per degree per molecule). This relationship is of the form of equation (8),

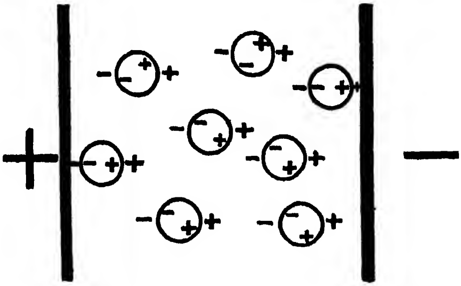


FIGURE LXIX.—Orientation of Polar Molecules in an Electric Field.

corresponding to decreasing " orientation polarization " with increasing temperature. Equation (18) represents $\frac{\epsilon - 1}{\epsilon + 2}\cdot\frac{T}{d}$ as linear with the absolute temperature T. According to Gans and Isnardi,[15,16] this only holds in the limiting case of high temperature and low density. A more complicated expression is developed by a statistical argument for ordinary conditions, according to which

$$P = \frac{\epsilon - 1}{\epsilon + 2}\cdot\frac{M}{d} = \frac{4}{3}\pi N\alpha + M\frac{A}{T}f(\tau) \ldots\ldots\ldots \quad (19)$$

where

$$\tau = \frac{T}{B}\cdot\frac{\sqrt{1 - \gamma d}}{\sqrt{d}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

where A, B and γ are molecular constants, and curves are given showing the relation between f(τ) and τ. According to this extension of the Debye theory, the function $(\epsilon - 1)T/(\epsilon + 2)d$

is linear with $T/\sqrt{d}$, or, more accurately, with $T\sqrt{1 - \gamma d}/\sqrt{d}$. The constant A involves M in the denominator, so that M disappears from the second term of (19).

Experimental data on the variation of molecular polarization with temperature has been provided by numerous workers already mentioned, Abegg and Seitz, Jona, Zahn, Gans and Isnardi, Sanger, Stuart and others (Chapter X). The general nature of the results is shown in Figures LX to LXIV. The Debye theory of the dependence of dielectric constant on temperature was questioned by Lyon and Wolfram[17] and by Bergholm.[18] These criticisms were answered by Lertes[19] in the light of the work of Debye, Gans and Isnardi, and Born.[20] The results upon which the remarks were based were shown to be in good qualitative agreement with the dipole theory and with the conclusions drawn by Gans and Born. van Vleck[21] has given a proof of Debye's equation (18) on the basis of the new quantum mechanics. The Debye theory thus rests upon a secure experimental and theoretical foundation.

It may be noted that gases near their points of liquefaction apparently deviate to some extent from the requirements of the Debye theory. It is found, for example, that deviations occur for *ethyl ether* in the critical state.[22] Zahn[23] reported departures in the case of *acetic acid* vapour at low temperatures and high pressures. It is found necessary to consider the influence of molecular vibration on the dipole moment, and Debye's theory can only be regarded as satisfactory if vibration is taken into account and the vapour is considered as a mixture of molecules statistically distributed among the vibrational states. van Vleck worked on the assumption that the moment is the same for all states of low energy.

It is observed in the preceding discussion that three independent lines of reasoning support the division of molecules into two classes, according as they possess dipole moment or not. In each of these cases, abnormally high polarizations may be associated with orientation polarization connected with intrinsic and permanent electric moment, the increase in P being accounted for by the added term in equation (18). Ammonia, for example, shows abnormality in all of these three ways, and must be definitely assigned to the polar Class II. The enhanced polarization increases P and therefore increases ϵ; hence departures from the Maxwell relation $\epsilon = r^2$ are found, which in turn affect the additivity of molecular refraction. The same cause evidently increases P above the value associated with the true volume of the molecules derived from van der Waals' equation, and by affecting the degree of orientation accounts for the variation of P with temperature. A list of some polar (Class II) and non-polar (Class I) molecules is given in Table XL.

TABLE XL.—POLAR AND NON-POLAR MOLECULES

	Molecules of Class I (Non-polar)	*Molecules of Class II* (Polar)
Physical Characteristics	(1) True volume of molecules approximately equal to molecular polarization.	(1) Molecular polarization greater than true volume of molecules.
	(2) Molecular polarization and molecular refraction additive	(2) Molecular polarization and molecular refraction show departures from additivity
	(3) Molecular polarization independent of temperature	(3) Molecular polarization decreases with increasing temperature.
Examples	A, H_2, N_2, CH_4, CCl_4, C_2H_6, C_2H_4, C_2H_2	HCl, HBr, HI, CO, CO_2, H_2O, H_2S, SO_2, N_2O, NH_3, PH_3, AsH_3, CH_3Cl, CH_2Cl_2, $CHCl_3$, CH_3 C_6H_5, C_2H_5OH, $C_2H_5O_2CH_3$

31. The Parts of Molecular Polarization

Molecular polarization is an additive function* for molecules of Class II, as appears from equation (18), where the first term on the right hand side corresponds to lack of rigidity in the molecule, whereby *deformation with induced moment* occurs in the presence of an external field, and the second to *orientation polarization*, connected with permanent molecular electric moment. When the deformation part of polarization is considered, it is also seen to be composite, consisting of two parts which may be termed " electron " and " atom " polarization respectively. *Electron polarization* P_E may be associated with the *shifting of electrons relatively to each other* under an external field, so that the centres of gravity of positive and negative charges no longer coincide. This is the deformation process to which Fajans has directed special attention. *Atom polarization* P_A may be regarded as an effect due to the *shifting of atoms, ions or radicals within molecules* under the influence of a field, thereby setting up an element of molecular asymmetry associated with induced electric moment. To these factors must be added the orientation polarization P_O taken up under an external field, the molecular polarization P being the sum of three terms as follows:

---

* The context will show that the word "additive" is here used in a different sense from that in the preceding paragraph.

$$P = P_E + P_A + P_O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (21)$$

Ebert[24] and Errera[25,26] have considered methods by which it is possible to separate P into its individual constitutive parts, and has shown that these parts depend differently upon the structure of the molecule in question. For example, the orientation polarization is practically constant in the series of normal aliphatic alcohols (this vol.: 38D). P_O corresponds to the second term of equation (18): the other term may be equated to $P_E + P_A$. So long as molecular refraction R is obtained from r_∞ calculated by extrapolation of r's in the visible region, we may set $R = P_E$; when measurements in the infra-red are included, then $R = P_E + P_A$. In this latter case, a different value of r_∞ is obtained from that derived from dispersion in the optical region of the spectrum. It now becomes necessary to examine the parts of equation (21) somewhat more closely.

(A) **Electron Polarization.** The most ready picture of polarization seems to be that in terms of waves of definite frequency, by which vibrations are set up in electrons, atoms or groups corresponding to the frequency of the radiation causing the effect. Electrons are light compared to atoms and molecular groups, so that relatively high-frequency vibrations will influence them. A free atom or ion may be perfectly unpolarized in the absence of a field, yet it has an inherent polarizability expressed by the constant α already considered. Electron polarization is noticeable in the visible and ultra-violet regions, and is most easily studied for these vibrational frequencies, which do not influence atoms or orient dipoles. P_E in general may be associated with R, the molecular refraction, known to be an additive property for atoms in organic homologous series. Electron polarization occurs in two connections, the effects concerned being not essentially different in nature:

(a) Under the influence of another ion, an ion may become deformed (Fajans' deformation process);

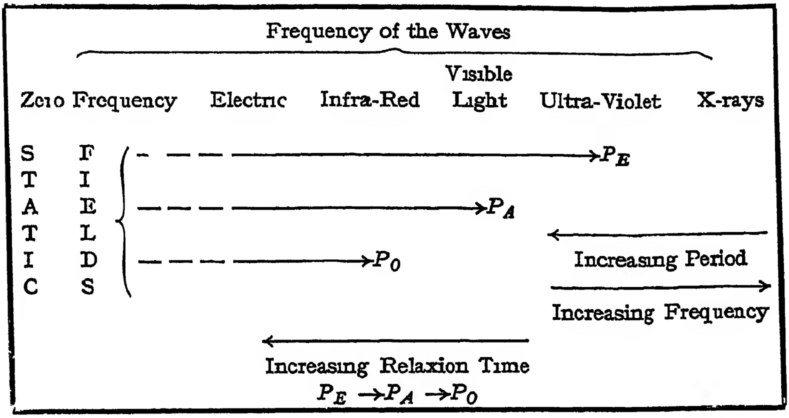
(b) Under the influence of a light wave, electrons may be set into natural periodic vibrations corresponding to the frequency of the light. Electron polarization is independent of temperature change.

(B) **Atom Polarization.** Atoms and radicals within molecules have natural vibrations dependent on temperature. Waves of lower frequencies than those of light, such as long infra-red waves, may set atoms, ions or groups within molecules in vibration, which becomes superimposed on the thermal vibration. Atom polarization is affected by temperature, but is rather less well understood than other types of polarization. Smyth[27] has deduced P_A values from the variation of dielectric constants of gases with temperature. The difference between molecular polarizations and molecular refractivities of *basic beryllium acetate* and *acetylacetonate*[28] is attributed to atom polarization. Sugden[29] has derived P_A's for a large number of substances, and has shown that for organic molecules the values are always small, about 0·1 of P_E. Jenkins[30] has conveniently summarized methods of determining atom polarization. It is probable that atom polarizations never exceed about 7 c.c.

(C) **Orientation Polarization.** When waves of a few centimetres' length strike a dipole, it tends to turn so that its axis lies along the direction of the field; this tendency is resisted by the translational and rotational movements of the molecule appropriate to the temperature of its surroundings.

The effect is to set the dipoles in vibration about an average mean position, so that the axes lie at some definite angle to the field direction. At very high temperatures, the effect of thermal movement is great, and hence the orientation polarization is correspondingly small.

The influence of wave frequency in causing the different kinds of polarization mentioned may be summarized as follows :


Frequency of the Waves
Zero Frequency
Electric
Infra-Red
Visible Light
Ultra-Violet
X-rays
STATIC
FIELDS
P_E
P_A
P_O
Increasing Period
Increasing Frequency
Increasing Relaxion Time
$P_E \rightarrow P_A \rightarrow P_O$

This representation of the facts shows the following three things :

(i) In the scale of frequencies, vibrations in the visible and ultra-violet regions will only cause electron polarization P_E ; such vibrations do not cause atom polarization and cannot orient dipoles. This provides the case $P_A = P_O = 0$ in equation (21), or $P = P_E$.

(ii) In the infra-red region, atom polarization P_A enters in, and electron polarization P_E is also set up, so that the total effect corresponds to the sum $P_E + P_A$. The frequency is too great to orientate dipoles, corresponding to the case $P_O = 0$, and $P = P_E + P_A$.

(iii) In the electric region, the orientation polarization effect represented by P_O commences, so that molecular polarization here contains all of the three parts in accordance with (21). Thus, for static fields, where the effect is the same as would be obtained by extrapolation to zero frequency (infinite wavelength), this equation is applicable.

It will be noted that overlapping of the parts occurs in the region of longer waves, and not at the other extreme. Thus electric waves give rise to electron polarization in addition to the other effects, although visible waves (of shorter period) cannot orientate dipoles. The natural frequency corresponding to P_E is less than for P_A and P_O, so that the time of one vibration, or "period," is least for P_E and greatest for P_O. Waves act as if capable of affecting that for which the natural period is less, and the natural frequency greater than their own. The relatively longer waves of the electric region have longer periods; thus a greater time elapses before the wave impinging on a molecule changes its phase. A dipole whose natural vibration, compared with that of an electron, is slow, can swing an appreciable distance from its mean position under the influence of a long electric wave before the wave changes its phase and sends it back again; a wave in the visible region changes its phase so quickly that it has no effect in causing orientation in molecular dipoles. Electron polarization is effective from the electric to the ultra-violet, because the natural periods of electrons are less than those of the waves throughout the region. As the periods of the waves are still further decreased, however, a state is reached in which the waves have shorter lengths and periods than those of electrons; so that X-rays cannot polarize at all, since they change phase too quickly even for electrons. Thus the facts are explained, and all three kinds of polarization enter into the case where the longer waves are employed.

The phenomenon of anomalous dispersion of dielectric constants at electric radio frequencies, associated with power loss by heating the medium, has been explained by Debye as a "relaxion" effect, whereby dipole orientation is not instantaneous, but requires a time interval commensurable with the time taken by the electric wave to perform one vibration (see this vol.: 27Ac). The relaxion time τ of a molecular sphere of radius r carrying a dipole varies with the viscosity η of the medium, and is given, within the limits of applicability of

Stokes' Law, by $\tau = 4\pi\eta r^3/kT$, where k is Boltzmann's constant, and T is the absolute temperature. Relaxion times of the order of 10^{-12} sec. occur. Debye[31] has recorded values of τ for o-*dichlorobenzene*, *nitrobenzene* and *chloroform* in *benzene* and other non-polar solvents. The results are confirmed to some extent by the fact that the molecular radii r come out, in accordance with expectation, to be of the order of an Ångstrom unit. Further examination of the results, however, shows that, for the same substance in different solvents, the r values may be different, and the relaxion times are not strictly proportional to the viscosities of the media. Hence Debye concludes that the picture of a molecular sphere is too simple for perfect agreement between theory and experiment to be obtained. Goldammer and Sack[32] have examined the applicability of Debye's expression for relaxion time in the case of *isobutyl alcohol* in *paraffin oil*. Kitchin and Müller[33] attempted to apply orientation polarization in explanation of anomalous absorption for fields whose frequencies were as low as 60 cycles per second: Hamburger[34] pointed out that this extension did not appear to be justifiable. Meyer[35] has emphasized the importance of "inner molecular potential," and finds that dipole rotation is prevented if this exceeds 0·1 of kT. The explanation of anomalous absorption for polar molecules in terms of orientation polarization constitutes one of the outstanding achievements of the Debye theory.

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CHAPTER XII

MOLECULAR REFRACTION

32. The Rule of Additivity

THE refraction of visible light is associated with induced atomic or molecular polarization which is independent of temperature. Electron polarization P_E enters in, and dipoles are unaffected. Molecular refraction R is defined by the Lorenz-Lorentz expression

$$R = \frac{r^2 - 1}{r^2 + 2}\frac{M}{d} = \frac{4}{3}\pi N\alpha \quad \dots \qquad \dots \quad (1)$$

where r is the index of refraction extrapolated to infinitely long waves. Sometimes, however, other values of R, such as those for the Na-D or H-α lines, may be conveniently used without serious error.

Crystals of the Orthorhombic, Monoclinic and Triclinic systems are said to be *biaxial*, and except in certain directions have three indices of refraction α, β and γ; in these cases, r for equation (1) may be taken as $\sqrt[3]{\alpha\beta\gamma}$. The Tetragonal and Hexagonal systems are *uniaxial*, and have two indices ω, ϵ, here $r = \sqrt[3]{\omega^2\epsilon}$. Cubic crystals have one refractive index only in all directions.

Other expressions of the form $R = XM/d$ have been suggested by Newton ($X = r^2 - 1$), Gladstone and Dale[1] ($X = r - 1$), Eykman[1] ($X = (r^2 - 1)/(r + 0.4)$), and Lichtenecker[1] ($X = \log r$). The Lorenz-Lorentz relation, having theoretical basis, is generally preferable.

The earlier work on molecular refraction as an additive and constitutive property was carried out mainly by Bruhl,[2] Landolt and Jahn[3], and Eisenlohr.[4] The last-named gave a table of atomic refractions and dispersions (1910), and afterwards (1912) extended the results to nitrogen compounds, which were shown to be peculiarly sensitive to changes in structure A summary of the early work up to 1912 was provided by Eisenlohr[5] More recently, Eisenlohr[6] has studied the molecular "refraction coefficient" $M\ r_D^{20°}$ as a constitutive property This work has been carried out mainly with reference to organic molecules

The interest of the more recent work on molecular refraction attaches to cases where departures from strict additivity are observed These have been related by Fajans to the influence of electronic deformation of outer shells of atoms and ions under the influence of neighbouring ions, and particularly to the influence of cations upon anions The idea of such deformation appears to have been first suggested by Haber,[7] in the models of the HCl molecule and of the Na atom In the case of HCl, Haber pictured a repulsion between the resultant charge of +7 (carried by the chlorine nucleus and two K and eight L electrons) and the +1 carried by the hydrogen nucleus, involving a displacement of the nuclei relative to the outer electronic system of the molecule Similarly, an attraction would exist between the outer electron of the sodium atom carrying charge −1 and the inner system carrying resultant charge +9 It is noteworthy, however, that some time earlier Kossel,[8] at the end of his lengthy treatise on the electrostatic basis of atomic and molecular structure, implied though did not state the existence of deformation in the models proposed for HCl, CaO and BN Haber considered the energy of union of a halogen ion to a hydrogen ion forming a hydrogen halide, and found it to be about 100 Calories greater than would be expected on the basis of rigid ions, and suggested that a shift of the nucleus of the halogen ion relative to its outer sheath might account for the result, the work done on combination being liberated as energy of deformation Reis[9] applied Born's theory of lattice energy to the solid hydrogen halides and studied the deforming working of the hydrogen ion on the halogen anions Born[10] considered deformation in relation to the results on residual rays, elasticity constants and piezo-electric constants Meisenheimer[11] related the colour of salts to deformation thus PbI_2 is yellow, though Pb^{++} and I^- are both colourless Weigert[12] studied the influence of deformation on optical and photochemical properties, and suggested that every chemical process may be regarded as a consequence of a primary polarization or displacement of an electron, whether the electron concerned returned to its parent particle or remained free was regarded as a secondary process not affecting the initial stage Debye[13] considered electric moment as a consequence of polarization, and treated molecular refraction as a measure of polarizability, on lines already explained Photochemical investigations on silver salts have been conducted by Frankenburger,[14] and by Fajans and collaborators[15,16] in relation to the deformation theory In addition, Born and Heisenberg[17] have treated deformation quantitatively in the way previously outlined Many of these investigations will receive further consideration in the present chapter

It is suggested in the theory of refraction that the refractivity of a molecule may be an additive function, such that

$$R = a_1R_1 + a_2R_2 + a_3R_3 + \qquad (2)$$

where R_1, R_2, R_3 , a_1, a_2, a_3 , are the individual refractions and numbers of atoms (or ions) constituting the molecule respectively The law was tested by Heydweiller,[18] who found it to be reasonably accurate for salts in dilute solution, and especially where deformation is absent Wasastjerna calculated the refractivities of ions of inert gas type from the data on the assumption that the refractivity of the hydrogen ion was zero If the hydrogen ion consists of a single proton, it may well be considered as undeformable Fajans and Joos,[16] however, threw some doubt on the validity of this assumption, adducing evidence of the existence of the hydrated ion H_3O^+ in aqueous solution, and preferred to fix the refractivity of the free gas ion Na^+ as 0 50, and thus to calculate values of other inert gas-like ions (see this vol 34A) The results obtained by the two methods are shown in Table XXXVI Spangenberg[19] determined the densities and refractivities of alkali halide crystals with accuracy, and showed that the additive law was not applicable to these substances in the solid state From the results of Fajans and Joos, and of Bragg,[20] who studied the effect of atomic arrangement upon refractive index, it seems to be clear that the values to be assigned to a_1, a_2, a_3 of (2) vary with the degree of dispersion and the environment of individual ions Fajans and Joos suppose the law to be strictly applicable to free gaseous ions

Havelock[21] has given formulæ for the refractivities of a number of polyatomic molecules in terms of those of the constituents, making allowance for their interaction on each other Born and Heisenberg[22] assumed that the valency electron of the alkali metals Li, Na, K was able to polarize the rest of the atom according to equation (4) of Chapter XI, and found that this results in an additional force of attraction of car^{-5}, where c is a constant for the metallic atom The constants for the Rydberg-Ritz formula of series spectra for Li^+, Na^+, K^+ were then obtained in terms of a, so that evaluation of the polarizabilities of these ions became possible by comparison with the computed spectral values of the constants The results are shown in Table XXXVII, where comparison is afforded with the corresponding numbers calculated from Wasastjerna's table of refractivities by means of equation (1)

Polarization by deformation provides two different cases, diagrammatically suggested in Figure LXX In case (a), the deformation is "one-sided," and the effect is similar to that of placing the molecule or ion between the plates of a condenser, as in (b), an induced dipole, having electric moment, being set up In this way, the permanent moment of the gaseous HCl molecule, for instance, may be explained as associated with the deformation of Cl^- by the hydrogen ion on one side The indication of band spectra is that the proton is embedded in the electronic system of the halogen In the second case (c), the deforming effect is "many-sided," and is such as may be expected to occur, for example, in an alkali halide crystal, where an ion is symmetrically surrounded by six neighbours Here there is no separation of the positive and negative charges, and although deformation occurs, there is no dipole set up, since the effect on one side is balanced by the effect on the opposite side, Figure LXX(c), due to Fajans,[23] must be regarded as purely illustrative and diagrammatic

Figure LXXI(a) shows two oppositely-charged ions of about equal size held together by electrostatic force (ideal polar linkage) In (b), the ideal homopolar case is depicted, in which the centres of gravity of positive and negative charges coincide Case (c) represents a case intermediate between (a) and (b), where a relatively small cation, having relatively large surface density of charge, is able to deform a larger anion, setting up an induced dipole The electrons on the outside of the anion have diminished freedom the system is said to be "stabilized,"

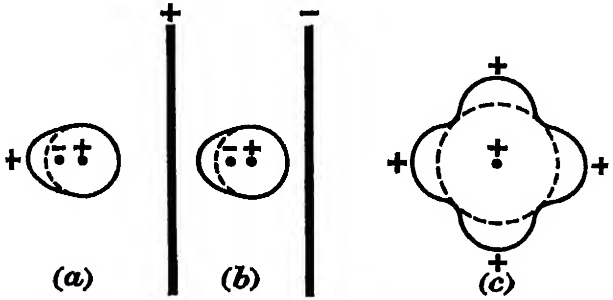


FIGURE LXX —One-sided and Many-sided Deformation Polarization

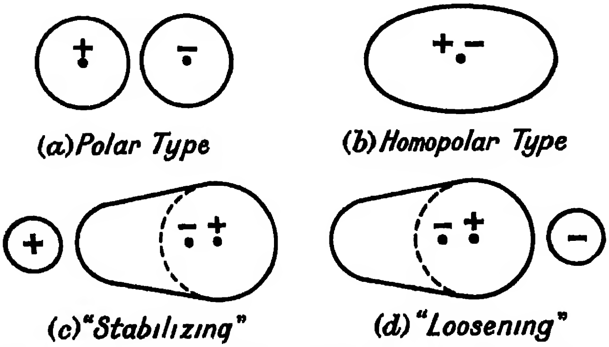


FIGURE LXXI —Polar and Homopolar Links Stabilizing and Loosening Effects and the electrons are less influenced by an incident light wave than would be expected on grounds of additivity The molecular refraction is therefore lowered Case (d) illustrates the influence of a small anion on a relatively large cation the outer electronic sheath of the cation is displaced in such a way that the centre of negative charge of the cation is driven away from the anion, with consequently diminished attraction and greater electronic freedom Hence the light wave has increased influence on the group, as compared with expectation on additivity grounds the system is said to be "loosened," and the molecular refraction is raised According to Fajans,[24,25] the smaller ions with higher charges have greater deforming power, whilst the larger and less highly-charged ions are more easily deformed Ions not of inert gas type are generally more strongly deforming than ions of inert gas type of the same size and charge (see following Section 33C)

The *dihydrate double sulphate* of *ammonium* and *calcium* follows the additive rule of molecular refraction of the constituent sulphates [26] The linear additive rule holds for mixed crystals in varying proportions of *magnesium sulphate* and *zinc sulphate*,[27] and of *silver bromide* and *silver iodide*,[28] but not of *thallium bromide* and *thallium iodide* [28] Deviations in the last-named case may be associated with strong deformation of iodine ions For compounds of similar type, where deformation is absent, molecular refractions of mixed crystals vary linearly with composition

An investigation on mixed salts in solution may be noted [29] In cases where no compounds are formed, as with NaCl-KCl and $NaNO_3$-KNO_3 mixtures, deviations from additivity rules may be associated with ionic deformation, compound formation is indicated by the appearance of maxima on the refractivity-composition curves, as in mixtures of $MgCl_2$-KCl (1 1), $MgCl_2$-NH_4Cl (1 1) and $CdCl_2$-KCl (1 1, 1 2 and 1 3) The numbers in brackets refer to the composition of compounds and the appearance of maxima

The refractive index of *nickel arsenide* may be calculated from a formula involving its reflective power in air and in cedarwood oil, together with the refractive index of the oil [30]

Parahydrogen has the same refractive index for the green mercury line as ordinary hydrogen [31]

33 Influence Factors on Deformation

The several factors influencing degree of deformation judged by departures from the additivity rule operate, in general, collectively, in what follows, an attempt is made to disentangle these factors, by considering the influence of one where the others change as little as possible

(A) **Influence of Nuclear Charge** Referring to Table XXXVI, it is observed that refractivity decreases for ions of the same type of outer structure as the nuclear charge increases

	O^{--}	F^-	Ne	Na^+	Mg^{++}
R	4 06	2 20	1 01	0 74	0 44
Z	8	9	10	11	12

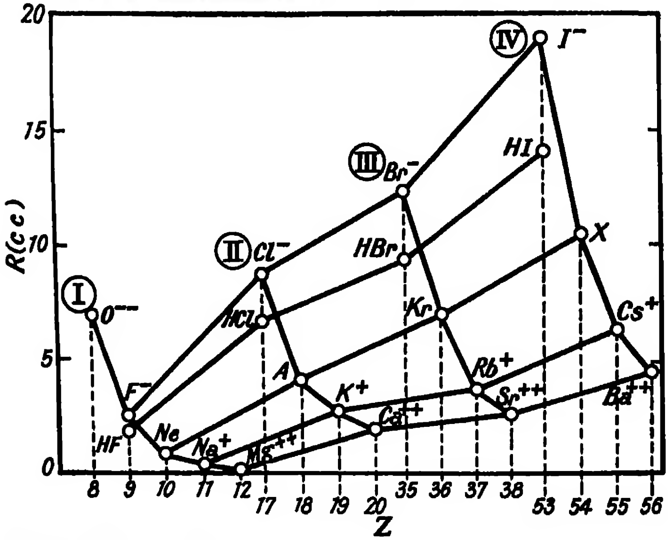


FIGURE LXXII — RELATION BETWEEN MOLECULAR REFRACTION AND NUCLEAR CHARGE

As the nuclear charge Z increases, the outer sheath of electrons is more firmly held, and the deformation and refractivity decrease Similar considerations apply to the other horizontal series of Table XXXVI Figure LXXII, due to Fajans and based on his estimates, shows this result quite clearly Thus the deformability of Mg^{++} is less than that of Na^+, the deforming power of Mg^{++} towards negative ions is correspondingly greater than that of Na^+, and similarly in other cases

(B) **Influence of Atomic Size** The vertical columns of Table XXXVI show that deformability and refractivity increase with increasing size (see also Figure LXXII) This accords with the views already expressed on the relation between polarizability and molecular volume Thus for the halogen ions

	F^-	Cl^-	Br^-	I^-
R	2 20	8 45	11 84	18 47
r	1 36	1 81	1 95	2 16

The radii of the ions are Pauling's estimates, taken from Vol 1 Table XXIX Thus deformability increases with increasing radius, and deforming power decreases Negative ions are in general more deformable than positive ions The ion F^-, however, being the least deformable, is most deforming, so that when associated with a more deformable cation, as Cs^+, Rb^+ or K^+ the loosening effect previously noted occurs, with an increase of molecular refraction This is illustrated by Figure LXXIII, due to Fajans[28] The curves, which are further explained below, are based on estimates of $R_{\text{crystal}} - R_{\text{free gas ion}}$, and show the loosening effect with increase of molecular refraction only in the cases of KF, RbF and CsF The same is observed with CaF_2, SrF_2, BaF_2 but not with MgF_2

Similar considerations hold for compounds of AX_4 type, for which results (for infinite wave-length) are given on page 288[32] The difference ΔR decreases from CCl_4 to $SnCl_4$ with increasing

AX_4	CCl_4	$SiCl_4$	$SnCl_4$	$SnBr_4$	SnI_4
$\frac{1}{4}R_{AX_4}$	6 47	7 05	8 65	11 93	17 53
R_{X^-}	8 73	8 73	8 73	12 13	18 12
ΔR	2 26	1 68	0 08	0 20	0 59

size of A from C to Sn, and ΔR increases from $SnCl_4$ to SnI_4 with increasing size (increasing deformability) of X from Cl^- to I^- The derivation of the estimates of R_{X^-} is considered in the sequel

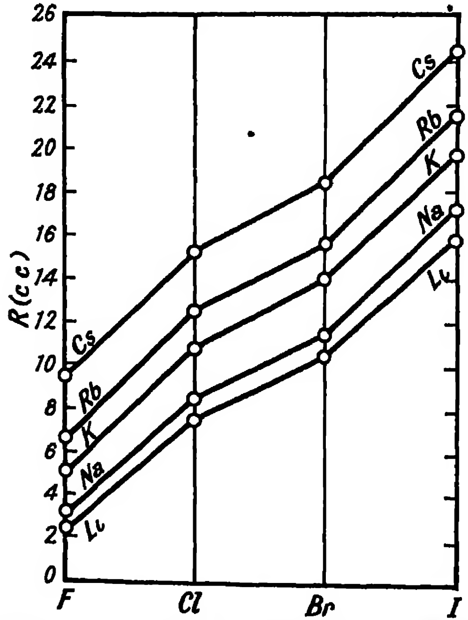


FIGURE LXXIII —MOLECULAR REFRACTION OF ALKALI HALIDES

Herz[33] found that for a large number of organic compounds the ratio R/b_e did not vary very much, b_e being the molecular volume calculated from the critical constants by means of the relation $b_0 = R'T_c/8P_c$, where R' is the gas constant Cuthbertson's empirical relation,[34] whereby the refractions from F_2 to I_2 and from Ne to Xe rise approximately in the ratio 1 6 9 14, may also be noted

(C) **Influence of Electron Sheath.** Ions not of inert gas type are more strongly deforming, other things being equal, than ions of inert gas type (see Vol 1 17C) Pauling[35] associates this with the greater electrostatic field within an outer shell of 18 as compared with that of 8 electrons The increased field is in accordance with the wave-mechanical view of atomic structure

Mention is made (Vol 1 17C) of the behaviour, noticed by Fajans,[36] of silver halides, as compared with sodium halides, where the cations are of approximately equal size, in respect of lattice distances and molecular volumes Referring to Tables VI, VIII and IX, the lattice distance differences d(NaX)-d(AgX) are (X = F) 4 62 − 4 92 = −0 30, (Cl) 5 63 − 5 54 = 0 09, (Br) 5 96 − 5 76 = 0 20, (NaI-AgIβ) 6 46 − 4 58 = 1 88, (NaI-AgIα) 6 46 − 6 47 = −0 01 Å U The effect of increasing deformation is to draw the ions together, diminishing lattice distance, thus the above differences increase from X = F (least deformable anion) to X = Br AgIβ has the wurtzite (B4) lattice, and AgIα the sphalerite (B3) lattice, the change from cubic lattices of AgBr and NaBr being marked by corresponding change in the sequence of differences In AgIα, the form stable above about 145°C, the effect of change of crystal structure is apparently compensated for by the increasing deforming power of Ag^+ as compared with Na^+

Similar considerations hold in respect of lattice energies,[36] defined as the energy set free when one gram-molecule of crystal is built up from free gas ions The following again affords comparison between sodium and silver halides U(NaX) − U(AgX) (X = F) 219 − 220 = −1, (Cl) 181 − 200 = −19, (Br) 168 − 193 = −25, (NaI − AgIβ) 156 − 188 = −32 kilogram calories The lattice energy of a crystal, calculated by Born's method, may be considered as the sum of three terms (1) a positive term, associated with work done by unlike charges in coming together, (2) a negative term, associated with work done by the repulsions of outer electronic sheaths of ions, (3) a positive term, corresponding to work done in deformation Terms (1) and (2) are probably not very different for sodium and silver halides, the progressively increasing differences from X = F to X = I may therefore be associated with relatively greater deforming power of Ag^+ as compared with Na^+ with increasing deformability of the anion

Fajans[37] has summarized more recent developments of the theory of deformation, and has pointed out that no means at present is known of estimating the refractions of free gas ions which are not of inert gas type It is possible, however, to draw certain conclusions without knowing these values, in the following way (calculations for Na-D line) We may compare two halides MX, MX′ of the same metal M in respect of deviations in the solid state from exact additivity fulfilled for the free gas ions Thus $\Delta R_{MX} - \Delta R_{MX'} = R_{MX} - (R_{M^+} + R_{X^-})_{gas} - [R_{MX'} - (R_{M^+} + R_{X'^-})_{gas}] = R_{MX} - R_{MX'} - (R_{X^-} - R_{X'^-})_{gas}$, where $R_{M^+ gas}$ is eliminated from the expression The following affords comparison between silver halides in this way

MX	R_{MX}	MX′	$R_{MX'}$	$R_{MX}-R_{MX'}$	X^-	$(R_{X^-})_{gas}$	X'^-	$(R_{X'^-})_{gas}$	$(R_{X^-}-R_{X'^-})_{gas}$	$\Delta R_{MX}-\Delta R'_{MX}$
AgBr	16.77	AgCl	13.50	3.27	Br^-	12.66	Cl^-	9.07	3.59	−0.32
AgI	23.77	AgBr	16.77	7.00	I^-	19.21	Br^-	12.66	6.55	+0.15

The differences in the deviations from additivity requirements become more positive between iodide and bromide than between bromide and chloride for Ag salts, and similar results hold for halides of other metals whose ions (*e g*, Hg^{++}, Sn^{++}) lack the inert gas structure Exactly the opposite is true for halides of metals whose ions are of inert gas type, the above-named differences becoming increasingly negative (see Table XLII)

Another way of demonstrating the peculiar behaviour of ions not of inert gas type in respect of departures of additivity in a series of halides is to subtract the contribution of the halogen ion free gas in each case from the equivalent refraction of the compound The following numbers refer to infinite wavelength, the refractions having been calculated from dispersion formulæ of the Sellmeier type, for gaseous halides of univalent K,[39] Ag[37] and Tl,[37,38] and bivalent Hg[39] and Sn [40] The differences ΔMX are of the type $R_{MX} - (R_{X^-})_{gas}$

X⁻	$R_{X\text{-gas}}$	R_{KX}	R_{AgX}	R_{TlX}	$\frac{1}{2}R_{HgCl_2}$	$\frac{1}{4}R_{SnCl_4}$	ΔKX	ΔAgX	ΔTlX	$\Delta\frac{1}{2}$HgCl$_2$	$\Delta\frac{1}{4}$SnCl$_4$	$\frac{1}{2}R_{SnX_2} - \frac{1}{4}R_{SnX_4}$
Cl	8 73	10 55	12 9	18 8	11 44	13 24	1 82	4 2	10 1	2 71	4 51	4 59
Br	12 13	13 37	16 1	22 3	14 63	16 61	1 24	4 0	10 2	2 50	4 51	4 71
I	18 12	18 78	22 3		20 78	(23 33)*	0 66	4 2		2 66	(5 21)	(5 80)

* Measurement on Na D line on account of dispersion

It is observed that the calculated differences for KX fall in the series from X = Cl to I, the same is true of the series SnX$_4$ (see table at end of 33A above) and of all series where the metal ion is of inert gas type Certain irregularities appear in the four following progressions ΔAgX, ΔTlX, $\Delta\frac{1}{2}$HgCl$_2$ and $\Delta\frac{1}{4}$SnCl$_4$, where the metal ions are not of this type The differences remain fairly constant in a series, and show no regular decrease The last column of the table[40] shows an increase per equivalent in passing from quadrivalent to bivalent Sn, with departure from inert gas type

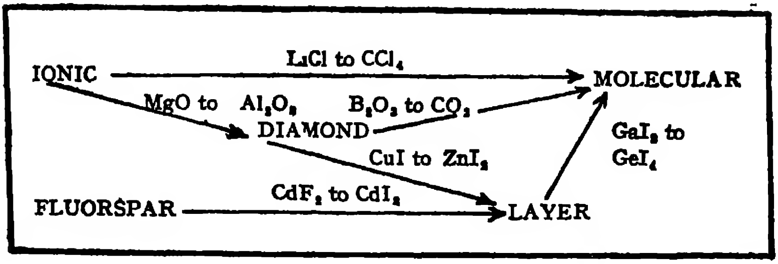
(D) **Effect of Number of Anions** According to considerations advanced in Section 32, the stabilizing effect accompanying anionic deformation is followed by a progressive lowering of molecular refraction (compared with the demands of the additivity rule) as the deformation increases In the following table, due to Fajans,[23] the contributions made by the halogen Cl or Br per atom are compared for molecules of the Type AX$_n$ (As shown on page 292)

The increase in the number of anions is accompanied by a progressive diminution in the contribution of each to the molecular refraction, and the values approach those for the given atom in the homopolar halogen molecule, shown on the right-hand side Increasing deformation occurs from left to

	LiCl	BCl$_3$	CCl$_4$	
R_{Cl}	7 4	6 97	6 61	R_{Cl} in Cl$_2$ 5 82
	NaCl	AlCl$_3$	SiCl$_4$	
R_{Cl}	8 0	7 68	7 01	
	LiBr	BBr$_3$	CBr$_4$	R_{Br} in Br$_2$ 8 72
R_{Br}	10 3	9 97	9 47	
	NaBr	AlBr$_3$	SiBr$_4$	
R_{Br}	11 1	10 9	10 2	

right, with development of homopolar characteristics The halogen atoms become more and more closely associated with the positive atoms, and the polar opposition between the ions of opposite sign becomes weakened In this way, the transition between the polar and homopolar linkages may be followed The appearance of the molecule as n increases in AX_n is associated with this neutralization of polarity and progressive "covering-up" of the central atom A Fajans also notes that the contributions of the chlorine atom in HCl and CCl$_4$ to the molecular refractions are approximately equal, being 6·67 and 6 61 respectively

(E) **Effect of Crystal Structure** The effect of deformation on crystal structure has been previously considered (Vol 1 17C and this vol 25C) Reference may be made to these discussions, in summary of which it may be said that increasing deformation favours the following transitions ionic to molecular, ionic to diamond, diamond to molecular, diamond to layer, fluorspar to layer, layer to molecular lattices. Examples, taken from Section 25C, are given above the arrows in the following scheme, the arrow directions showing those of increasing deformation


IONIC
LiCl to CCl₄
MOLECULAR
MgO to Al₂O₃
B₂O₃ to CO₂
DIAMOND
GaI₂ to GeI₄
CuI to ZnI₂
CdF₂ to CdI₂
FLUORSPAR
LAYER

Deformation is thus linked with the development of molecular, or homopolar character The diamond and layer lattices may be regarded from this point of view as intermediate stages in the change It is to be noted that in these cases it is the anion which undergoes progressively increasing deformation, the stabilizing process previously noted being thus accompanied by loss of polarity

Fajans[23] has considered the effect on molecular refraction in the transitions RbCl to CsCl and BeO to MgO, quoting the following figures

Substance	RbCl	CsCl	BeO	MgO
Crystal Type	NaCl	CsCl	ZnS-α	NaCl
Designation	B1	B2	B4	B1
$R_{\text{Free gas ions}}$	12 84	15 60	7 1	7 3
R_{Crystal}	12 55	15 22	3 28	4 53
Diminution	−0 29	−0 38	−3 8	−2 8
No nearest neighbours of negative ion	6	8	4	6

An increasing diminution of molecular refraction in passing from RbCl to CsCl occurs, as derived by subtracting the values found for the crystals (calculated from their indices of refraction) from those for the free gas ions (obtained from measurements in solution and extrapolation to infinite dilution) It is clear that an increase in degree of co-ordination from 6 to 8 for the chlorine ion is accompanied by a greater departure from the additivity rule, as based upon the values assigned to the free gas ions This occurs in spite of the increased lattice distance in passing from RbCl to CsCl (3 29 to 3 56 Å U), which would be expected to operate in the opposite direction were it not for the change in structure In the transition from BeO to MgO, however, an increase in co-ordination from 4 to 6 is accompanied by a reduced lowering of molecular refraction as judged by the same standards

Hund[41] has shown by a mathematical argument that where the crystal ions have small polarizabilities, ionic co-ordination lattices tend to be formed , greater polarizability is associated with the appearance of layer or molecular lattices van Arkel[42] has considered the polarization energies of crystals of NaCl, ZnS and CsCl types, and has shown that their relative magnitudes depend upon the radius ratios of the ions concerned Thus, for a radius ratio r_M/r_X less than 0 7, the polarization energies of ZnS, NaCl and CsCl types decrease in the order named, whereas, for radius ratios greater than this limiting value, the order is reversed This when considered in the light of Goldschmidt's work on the influence of radius ratio on crystal structure (see Table XXXI and accompanying text) is used to explain why some crystals within the correct limits of radius ratio for a given type according to the theory do not always crystallize according to that type Goldschmidt himself emphasized the influence of polarization as a factor in the determination of crystal structure The allowance to be made for polarization fields in crystals as calculated by Lennard-Jones has been already mentioned in Vol I 33 The value of Born's repulsion exponent n (equation (2) of Vol I 19) for crystals of different types is also important in the present connection

34 Applications of Refractivity Data

Examination of the literature shows considerable divergence in some cases between the values calculated by different investigators for the polarizabilities of ions, and these are not known in general with great accuracy Moreover, it appears that the relation $m = aF$ (equation (4) of Chapter XI) is inapplicable to very strong fields such as obtain between an atomic core and a valency electron No very great importance, however, need be attached to the absolute values of polarizabilities from the present point of view, since the orders of magnitude (relatively large or small) and the directions (increasing or decreasing) of the changes of molecular refraction in passing from one member to another in a series of related compounds may still be followed with respect to corresponding changes of molecular structure

(A) **The Alkali Halides and Hydrides** According to the results of Spangenberg,[19] additivity of molecular refraction in terms of constituent ions is lost for the alkali halides in the solid state Fajans and Joos[16] considered that strict additivity should be observed both for the free gas ions and for ionic refractions in aqueous solution extrapolated to infinite dilution Three quantities are therefore considered

(1) the additive refraction of free gas ions ,
(2) the additive refraction of ions at infinite dilution in aqueous solution ,
(3) the non-additive refraction of the solid salts

It then appears that (1) is unequal to (2) where highly deforming ions of small radius are present, because these ions deform the outer sheaths of water molecules, with consequent change in the refraction of the solvent Where the small deforming ion is a cation, as Li^+ and Na^+, a smaller value is obtained for (2) than for (1) , where it is an anion, (2) is greater than (1) , where both kinds of ions are present, as in LiF and NaF, the result will depend on whether the effect of the cation outweighs that of the anion or not. These considerations are in accordance with the views expressed in Section 32 above For other univalent ions, K^+, Rb^+, Cs^+, Cl^-, Br^-, I^-, the difference between (1) and (2) is found to be very small

In order to form estimates of departures from additivity of ions in the solid state, it is necessary first to estimate the refraction contributions of the free gas ions This matter is considered in Section 30A Fajans[87] used the Cuthbertsons' data on refractions of inert gases, the measurements of Heydweiller on solutions, and those of Spangenberg on solids It was assumed that for the gaseous state

$$\frac{R_{O^{--}}}{R_{F^-}} > \frac{R_{F^-}}{R_{Ne}} > \frac{R_{Ne}}{R_{Na^+}} > \frac{R_{Na^+}}{R_{Mg^{++}}} ,$$

and the upper and lower limits for $R_{Na^+_{gas}}$ were thus fixed at 0.72 and 0.39, the intermediate value 0.48 c c has been chosen Similar reasoning gave corresponding values for Li^+ and F^- of 0.20 and 2.44 c c respectively From Heydweiller's measurements, it was deduced that $R_{Na^+_{soln}}$ at infinite dilution was 0.20, the argument, however, does not rule out greater values than this, and Fajans has also used 0.35, the values corresponding to this second number being omitted here Further details of the derivation of these numbers will be found in Fajans' memoir[87]

TABLE XLI—REFRACTIONS OF UNIVALENT INERT GAS TYPE IONS (Fajans) (Na-D, c c)

	Li^+	Na^+	F^-	OH^-	K^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
R_{gas}	0.20	0.48	2.44	4.76	2.26	3.79	6.54	9.07	12.66	19.21
R_{soln}	−0.33	0.20	2.60	5.10						
$R_{soln} - R_{gas}$	−0.53	−0.28	+0.16	+0.34	very small			very small		

The difference values of Table XLI give the effect of the ions on the molecular refraction of water The influence of Li^+ is greater than that of Na^+, since Li^+ is smaller and more deforming, F^- and OH^- have increasing positive differences, corresponding to repulsion of the outer sheaths of water molecules due to the negative charges, thereby increasing the refraction of the solvent The other ions have very small, generally negligible, effects

Fajans holds that the above estimates are in satisfactory agreement with comparable results of other authors In particular, Pauling,[43] using shielding constants, deduced the following R_{gas} values K$^+$ 2 11, Na$^+$ 0 46, Cl$^-$ 8 86

Proceeding upon the assumption of additivity for R_{gas} and R_{soln} at infinite dilution, it is possible to calculate values for halide salts For LiF, $R_{soln} = -0\ 33 + 2\ 60 = 2\ 27$, $R_{gas} = 0\ 20 + 2\ 44 = 2\ 64$, and so on in other cases The numbers given in Table XLII are based upon Fajans and Joos' earlier estimates, and therefore may be slightly different from those deduced from Table XLI, but the orders of magnitude and directions of change are practically unaffected

Newman[44] has recently measured R_{soln} for NaCl for infinite dilution (Na-D, 18°C), and obtains 9 05 c c (compare 9 20 from Table XLII) In other cases, especially with Rb$^+$ and Cs$^+$ salts, some of the numbers obtained using the constants of Table XLI show discrepancies with numbers in Table XLII Thus Wulff and Heigl[45] obtain the following $R_{cryst} - R_{gas}$ values KCl —0 47, RbCl —0 29, CsCl —0·40 , NaF 0 02, KF 0 43, RbF 0 47, CsF 0 48

In solution, the refractions of ions are different from their values in the gaseous phase in cases where deformation of water molecules occurs no interaction between ions of opposite sign will normally take place In LiF, the elevating effect of Li$^+$ is greater than the diminishing effect of F$^-$ upon water, and there occurs a net decrease in molecular refraction from 2 70 to 2 38, that is, of 0 32 (Table XLI gives —0 53 (Li) + 0 16 (F$^-$) = —0 37) With NaF, the cationic and anionic effects about neutralize each other, and so $R_{gas} = R_{soln}$ The influence of F$^-$ acting alone is seen in KF, RbF and CsF Similarly, in LiCl, LiBr and LiI, the effect is due to Li$^+$ only, and there is a constant difference $R_{soln} - R_{gas}$ of —0 62 Similar considerations hold for NaCl, NaBr and NaI, where the difference is 0 30 due to Na$^+$ In all other cases, $R_{gas} \neq R_{soln}$

TABLE XLII.—MOLECULAR REFRACTIONS OF THE ALKALI HALIDES (Na-D, c c, 20°C)

Six numbers are given in each partition of the table the first three, from the top downwards, are R_{gas}, R_{soln}, and R_{cryst}, the second three are the differences $R_{soln} - R_{gas}$, $R_{cryst} - R_{soln}$, and $R_{cryst} - R_{gas}$ respectively. R_{cryst}, is the experimental value deduced from measurements of indices of refraction of solid salts The values of R_{soln} are in agreement with the values of Heydweiller extrapolated to infinite dilution

	Fluoride		Chloride		Bromide		Iodide	
	R	Δ	R	Δ	R	Δ	R	Δ
Lithium	2 70	−0 32	9 20	−0 62	12 87	0 62	19 14	0 62
	2 38	−0 04	8 58	−0 99	12 25	−1 69	18 82	2 84
	2 34	−0 36	7 59	−1 61	10 56	− 2 31	15 98	3 10
Sodium	3 00	0 00	9 50	−0 30	13·17	0 30	19 71	0 30
	3 00	+0 02	9 20	−0 68	12·87	1 31	19 44	2 37
	3 02	+0 02	8 52	−0 98	11·56	1 61	17 07	2 67
Potassium	4 73	+0 30	11 23	0·00	14 90	0 00	21 17	0 00
	5 03	+0 13	11 23	−0 38	14 90	0 92	21 47	1 72
	5 16	+0 43	10 85	−0 38	13 98	−0 92	19·75	1 72
Rubidium	6 08	+0 30	12 58	0 00	16 25	0 00	22 82	0 00
	6 38	+0 36	12 58	−0 03	16 25	− 0 47	22 82	1 11
	6 74	+0 66	12·55	−0·03	15 78	− 0 47	21 71	1 11
Caesium	8 74	+0 30	15 24	0 00	18·91	0 00	25 48	0 00
	9 04	+0 47	15·24	+0 01	18·91	−0·45	25 48	1 21
	9 51	+0 77	15·25	+0 01	18 46	−0·45	24 27	− 1 21

in accordance with the postulated negligibly small influence of all ions of the series excepting Li^+, Na^+ and F^-

In the solid state, additivity is lost and interaction between the ions ("many-sided" deformation) takes place, and the differences $R_{cryst} - R_{gas}$ may be taken as a measure of this effect In LiF, the effect of the smaller Li^+ upon F^- is greater than the reverse effect, so there is a net lowering of refraction

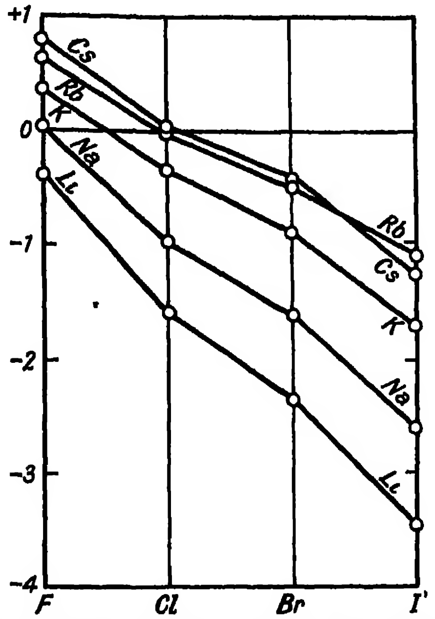


FIGURE LXXIV—PLOT OF $R_{crystal} - R_{free\ gas\ ions}$ FOR ALKALI HALIDES (Fajans)

from 2·70 to 2·34 = −0·36 Proceeding in the series NaF to CsF, the negative influence (loosening, giving increased contribution to refraction) of F^- becomes increasingly noticeable as the sizes and deformabilities of the cations increase For other halides than fluorides, from lithium to cæsium salts, the effects are stabilizing on anions, and the differences decrease from Li^+ (smallest, most deforming) to Cs^+ Certain abnormalities appear with CsCl, CsBr and CsI, which may be associated with the different structural arrangement (see 33E above) of these crystals (body-centred cubic) Thus there is an increasing difference $R_{cryst} - R_{gas}$ in passing from RbI to CsI, and the cæsium salts run closer to the rubidium salts than would be expected from the sequence in the series of chlorides and bromides Reference may be made to Figures LXXIII and LXXIV, which show the refractions of the solid salts and the differences $R_{cryst} - R_{gas}$ as estimated by Fajans The refraction, as well as the refraction difference, is greatest in the case of LiI, where the most easily deformed anion is associated with the most deforming cation

The figures for the solid salts have found certain quantitative significance [46] Born and Heisenberg[17] showed that the energy of a dipole induced in one ion by another varies inversely as the fourth power of the distance between the two ionic centres, a proof of which is given in the appendix to Chapter XIV Fajans proposed the following empirical relationships

$$\Delta R_X = \frac{k_X}{d^4} = C\,\frac{R_X^2}{d^4} \qquad . \quad . \qquad (3)$$

where ΔR_X is the diminution in refraction due to deformation of an anion, k_X is constant for a given anion, d is the semi-lattice distance, C is a constant for all anions and R_X the refraction due to the gas anion

Further, if

$$\Delta R = R_{cryst} - R_{gas} = \Delta R_M + \Delta R_X \qquad (4)$$

where ΔR_M is the elevation of refraction due to deformation of cation by anion, the appropriate signs for ΔR_M, ΔR_X being observed The relation (3) may now be tested for LiCl, LiBr, LiI and NaI, on the assumption that $\Delta R_M = 0$ in these cases, so that $\Delta R_X = R_{cryst} - R_{gas}$, as found from Table XLII Then, for example, for LiBr, $C = R{\cdot}d^4/R_X^2 = -2\ 31 \times (2{\cdot}74)^4/(12\ 67)^2 = -0\ 81$, whilst for NaI, $C = -2\ 67 \times (3\ 23)^4/(19\ 24)^2 = -0\ 78$, the corresponding values for LiCl and LiI being $-0\ 86$ and $-0\ 78$ respectively This constancy of C within the probable error indicates the validity of equation (3) to these cases Assuming this, it is possible to proceed a little farther, and apply the values of k_{Cl^-}, k_{Br^-} and k_{I^-} found to other halides where ΔR_M cannot be neglected, the value of k_{F^-} being obtained from $C\,R^2_{F^-} = (2\ 5)^2C$, where $C = 0\ 82$ (mean value) Using these k values, values of ΔR_X may be estimated in other cases, and thus ΔR_M may be deduced using equation (4) It is found that ΔR_M increases for a given cation with decreasing lattice distance, and with different cations according to their deformabilities, in accordance with expectation

Errera[47,48] measured the dielectric constants of solid alkali halides, and so calculated the total molecular polarization P by the Clausius-Mosotti formula This $P = P_E + P_I$, where P_E denotes the part due to electrons (equal to the molecular refraction R obtained from Spangenberg's measurements extrapolated to infinite wave-length, and inserted into the Lorenz-Lorentz expression), and P_I (obtained from $P_I = P - P_E$) the part due to ions The quantity Q, defined by $(\epsilon - r_\infty{}^2)/(\epsilon - 1)$, measures the proportion of total polarization due to ions The calculation shows that Q and P_I/P are greatest for LiF and least for RbI in the series of halides from Li^+ to Rb^+ Thus the ionic polarization is greater the greater the radii and the deformabilities of the ions concerned

Wasastjerna[49] has considered atomic and ionic refractions in relation to the electron distributions by wave mechanics, and finds that for an ion of inert gas type P_I is nearly proportional to the fourth power of the mean distance of the outer ring of electrons from the nucleus

Ammonium halides have been studied from the standpoint of deviations from additivity of molecular refractions [50] The values of $R_{NH_4X(cryst)} - (R_{NH_4^+} + R_{X^-})_{gas}$ are (X = F) $+ 0\ 38$, (Cl) $- 0\ 78$, (Br) $- 1\ 18$, (I) $- 1\ 30$ The value of $R_{NH_4^+\,gas}$ is estimated as 4 30 c c The departures from additivity follow the same rules as in the case of alkali halides In NH_4F, a proton of NH_4^+ is displaced towards the F^- ion ("contra-polarization"), but the displacement is insufficient to produce a molecular lattice (see 34Dc) No displacement occurs for the other halides As with Cs salts, an intensification of the refraction effect is observed on passing to a lattice of higher co-ordination number (NH_4F to NH_4Cl)

The refractions of NaH and KH have been measured for the

Na-D line,[51] the results being in fairly close agreement with estimates made by Herzfeld and Wolf,[52] as follows R_{NaH} 4 84 (obs) 4 40 (calc), R_{KH} 7 36 (obs) 7 53 (calc) The contribution made by H^- is 4 84 − 0 48 = 4 36 in NaH and 7 36 − 2 26 = 5 10 in KH (using refractions of gas ions from Table XLI) As an anion, H^- thus exhibits considerable deformation, and falls between F^- and Cl^- in this respect

(B) **Compounds containing Polyvalent Inert Gas Type Ions** Bivalent ions, other things being equal, may be expected to be more efficient deformers of water molecules than univalent ions, and tervalent than bivalent ions Some results are in Table XLIII, the R_{gas} values being obtained by the approximation method previously described for univalent ions [37]

TABLE XLIII—REFRACTIONS OF BIVALENT AND TERVALENT INERT GAS IONS (Na-D)

	Mg^{++}	Ca^{++}	Sr^{++}	Ba^{++}	Al^{+++}	La^{+++}
R_{gas}	0 26	1 40	2 58	4 73	0 17	3 3
R_{soln}	−1 80	0 71	1 89	4 37	−2 41	1 4
$R_{\text{soln}} - R_{\text{gas}}$	−2 16	−0 69	−0 69	−0 36	−2 58	−1 9

The absolute values of the differences decrease from Mg^{++} to Ba^{++}, and from Al^{+++} to La^{+++}, show decrease with increasing size of cation, in accordance with theory Comparison between this and Table XLI shows the more highly-charged ions to be more efficient deformers this is further indicated in Figure LXXII Values for R_{gas} for negative bivalent ions are O^{--} 6 95, S^{--} 22 7, Se^{--} 28 8, Te^{--} 40 9

The values of $\Delta R = R_{\text{cryst}} - R_{\text{gas}}$ in the series from BeO to BaO are found to be BeO −3 2, MgO −2 8, CaO −0 9, SrO −0 2, BaO +1 3 In BaO, the effect of O^{--} upon Ba^{++} is greater than the reverse effect The lowerings of R for oxides, sulphides, selenides and tellurides of bivalent metals are plotted in Figure LXXV, as given by Fajans,[25] in 1928, Wulff and Heigl[45] find the following ΔR values MgF$_2$ −0 44, CaF$_2$ +0 06, SrF$_2$ +0 52, BaF$_2$ +0 80, CaCl$_2$ −3 4, SrCl$_2$ −1·64, BaCl$_2$ −1 06 The positive effect of F$^-$, as well as the influence of change in crystal structure between MgF$_2$ (C4 type) to CaF$_2$ (C1 type) with increasing degree of co-ordination, is well marked Wulff and King[53] give for the Na-D line the following values of ΔR PbCl$_2$ −1 0, PbBr$_2$ −0·30, Sr(NO$_3$)$_2$ −1 0, Ba(NO$_3$)$_2$ +0·08, Pb(NO$_3$)$_2$ −0 68, CaSO$_4$ −0 74, SrSO$_4$ −0 8, BaSO$_4$ −0 4, PbSO$_4$ −2 4 Sr^{++} shows stronger refraction effect than Ba^{++}, CaSO$_4$ has different crystal structure from SrSO$_4$, the co-ordination number of Ca^{++} being 4, and of Sr^{++} 7 In the isomorphous series of bivalent nitrates, the radius of the Pb^{++} ion is about equal to that of Sr^{++}, but Pb^{++} has the larger number of electrons, and is not of inert gas type, so that its deforming power is

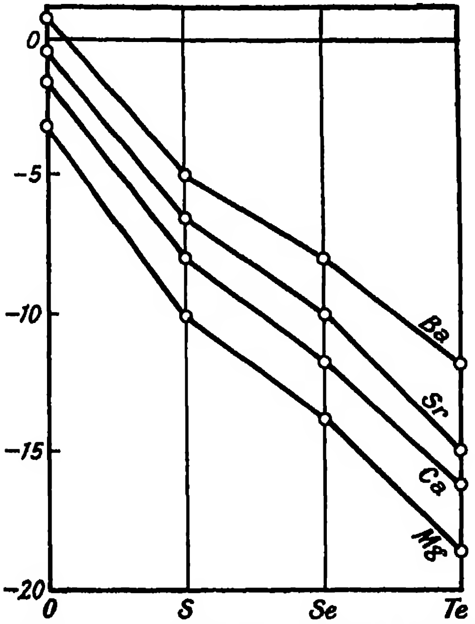


FIGURE LXXV.—PLOT OF $R_{\text{crystal}} - R_{\text{free gas ions}}$ FOR BIVALENT COMPOUNDS OF MgO TYPE correspondingly increased. Similar views are expressed by Errera and Brasseur.[54] The AlX_3 halides[55,56] show ΔR increasing in absolute amount from X = Cl (−3·79) to Br (−5·15) with increasing deformability of X. When X = I, the value is anomalous (−4·29), which may be due to the action of homopolar forces. The alums[57] have also been discussed.

(C) **Organic Compounds.** The contribution of CH_2 to molecular refraction in *normal paraffins* is strictly additive and equal to 4·60; the paraffins have zero dipole moment, and show a slight increase of polarization with temperature.[58] The refractive indices of *ethyl esters of normal fatty acids* and of higher *aliphatic alcohols* (C_5 to C_{10}) have been determined at 15°, 20° and 25°C.[59] The contribution of F in organic compounds has been computed as 1·09 for the Na-D line, from measurements on *benzyl fluoride*.[60] Schiemann[61] has obtained the lower value 0·997 from measurements on 30 aromatic compounds.

Puschin and Matavulj[62] have examined the departures from additivity of liquid mixtures containing *acetic acid* and various *amines*, and have found evidence of compound formation. Further work[63] indicated a decrease in degree of association of *phenols* and *amines* on solution in *benzene*. The refractive indices of liquid mixtures of *pyridine* and *phenols*[64] indicate the formation of compounds of the same composition as in the solid state.

Widmer[65] has found the following molecular refractions of alkali metal X *hydrogen phthalates*: X = Na 40·92, K 43·04, Rb 44·53, Cs 47·82, Am 44·97.

Some further contributions to the well-known constitutive influences on molecular refraction of compounds may be noted. Leithe[66] has shown that the atomic refraction contributions of halogens increase with the number of halogen atoms attached to a given carbon atom. The values for 1·2 substituted derivatives are different from those of 1·3. Errera[48] examined the dielectric constants of *cis*- and *trans*-CHBr : CHBr. The liquid cis-compound, which is polar, showed a drop in ϵ on solidification from 6·62 to 2·64, which is about the same as the value for the liquid non-polar trans-compound (2·72). Stieger[67] has evaluated the contribution of N to molecular refraction as 2·322 for primary, 2·499 for secondary, and 2·840 for tertiary amines. v. Auwers[68] has further determined the refraction equivalents of carbimic and iminic N for the Na-D line, as follows: O-N=C 3·901, H-N=C 3.05, N-N=C 3·46; C-N-C 4·10, N-CO-R 2·606, N-CO-OR 2·32. This author[69] advocates the use of "specific refraction" (equal to R/M) in studying the influence of conjugation and the presence of certain groups, as being independent of molecular sizes, and thus yielding comparable numbers, in opposition to the view of Hückel[70] v. Auwers[71] has recently discussed the specific refractions of a large number of derivatives of *pyridine*, in connection with the structural influences of different groups.

It is found that the semi-polar bond in molecular structure exerts a depression of molecular refraction of from 0·2 to 0·5.[72,73] The results appear unfavourable to the "donor-acceptor" theory (see this vol.: 40) of the *association of alcohols*. Double molecules of *acetic acid* in *benzene* have the same molecular refraction as single molecules in *dioxane*.[74] Work on these lines has been extended to solutions of *chlorobenzene*, *bromobenzene*, *phenol*, *aniline*, *dimethylaniline*, *anisole* and *benzonitrile* in *benzene*.[75]

The relations between the refractive indices and the behaviour of cellulose fibres has been discussed by Preston.[76]

(D) **Refraction of Complex Groups.** (a) *Groups containing Oxygen.* The contribution of complex ions containing oxygen to molecular refraction is generally much greater than that assigned to the free gas ion O^{--} (7·0). When the total oxygen contribution is divided by the number of atoms, however, it is found that there is a lowering of refraction contribution *per linkage*. Some results are in Table XLIV. The figure in the R line gives the refraction to be attributed to the group, derived from measurements of indices of refraction (D line) of pure substances with any requisite allowance for the presence of other ions or groups. For example, perowskite $CaTiO_3$ gives $r = 2·38$, $d = 4·0$, whence $R = 20·7$ by the refraction formula. Subtracting $R_{Ca^{++}} = 1·4$ (Table XLIII), $R_{TiO_3^{--}} = 20·7 - 1·4$ –

19·3, and similarly in other cases. The next line contains the correction R_A made for the central atom A of the group. The differences are then divided by the number of oxygen atoms to give refraction per linkage. Finally, this number is subtracted from $O^{--}_{gas} = 7·0$, to give the lowering of refraction per oxygen atom on account of deformation by the central positively-charged atom. Kossel's view of the electrostatic constitution of the groups is provisionally adopted. The corresponding figures for certain oxides are inserted in the Table for comparison.

In the series CO_3^{--}, SiO_3^{--}, TiO_3^{--}, the charges on the central atoms are constant (+4) but the central atoms increase in size. This is accompanied by diminishing deformation of O^{--}, and the lowering of refraction falls from 2·92 to 0·8. The same applies to SO_4^{--}, CrO_4^{--}, the latter being the more polar of the two. Considering next the series SiO_3^{--}, PO_4^{---}, SO_4^{--}, ClO_4^-, the charge on the central atom increases from +4 to +7, and the lowerings of refraction due to deformation of O^{--} increase from 2·58 to 3·70, associated with the increase of charge. The lowering per O^{--} in CO_2 is approximately the same as in ClO_4^-, indicating the same kind of linkage in the two cases. A similar comparison may be made between SO_3 and SO_4^{--}. Deformation is linked with a loss of polarity in these cases, so that the linkages lie between the polar and homopolar extremes. The figures in the bottom line of Table XLIV are thus a measure of departure from strictly polar constitution (in Kossel's sense) of these groups.

The four modifications of *ammonium nitrate*[77] have been found to have the same refractive indices when reduced to conditions of equal density; the angles calculated between the valency directions agree with the X-ray results.

(b) *Groups containing Hydrogen.* As previously noticed, Wasastjerna assumed the refraction contribution of H^+ to be zero. Fajans and Joos,[16] however, calculated $H^+_{soln} = -0·67$, by subtracting the refractions of anions from those of acids in solution. The molecular refraction of water (Na-D line, 20°C.) being 3·71, that of the ion OH_3^+ is given by $3·71 - 0·67 = 3·04$.

TABLE XLIV—REFRACTION OF MOLECULAR GROUPS CONTAINING OXYGEN.
(AO_n type—D line—Fajans.)

Group	CO_3^{--}	SiO_3^{--}	TiO_3^{--}	NO_3^{-}	PO_4^{---}	SO_4^{--}	CrO_4^{--}	ClO_4^{-}	CO_2	SiO_2	TiO_2	SO_3
Valency of A	+4	+4	+4	+5	+5	+6	+6	+7	+4	+4	+4	+6
R	12·27	13·37	19·3	11·00	16·30	14·84	26·80	13·25	6·68	7·22	13·0	11·01
R_A	0·03	0·10	0·6	0·02	0·07	0·05	0·40	0·04	0·03	0·10	0·6	0·05
Diff	12·24	13·27	18·7	10·98	16·23	14·79	26·40	13·19	6·65	7·12	12·4	10·96
R_o (per O^{--})	4·08	4·42	6·2	3·66	4·06	3·70	6·60	3·30	3·33	3·56	6·2	3·65
Diff from O^{--}_{gas}	2·92	2·58	0·8	3·34	2·94	3·30	0·40	3·70	3·67	3·44	0·8	3·35

This value is included in Figure LXXVI, where the refractions of various groups are plotted against numbers of hydrogen atoms. The results show the progressive lowering of refraction accompanying the laying-on of successive hydrogen ions; thus in the series O^{--}, OH^-, OH_2 (vapour), OH_3^+, the values are 7, 5·1, 3·76, 3·04 respectively. A similar effect occurs between

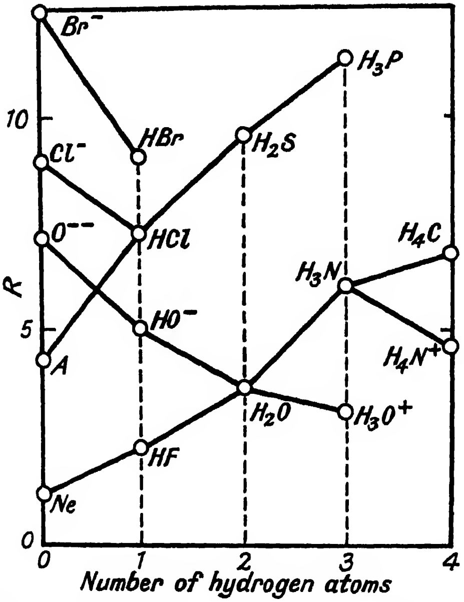


FIGURE LXXVI.—REFRACTION OF GROUPS CONTAINING HYDROGEN. The molecular refractions are plotted against numbers of hydrogen atoms present in the molecule.

NH_3 and NH_4^+, where the values are 5·61 and 4·13. The ions Rb^+, OH_3^+, NH_4^+, do not differ greatly in refraction values and resemble each other in other ways (see Vol. I: Table XXV). The refraction of CH_4 resembles that of Kr (see Vol. I: Table XXVII). The refraction values of HCl, HBr and HI in Figure LXXVI are taken from the measurements of Cuthbertson :[78] 6·67, 9·14 and 13·74 respectively, whence, subtracting the halogen ion values of Table XLI, the hydrogen makes negative contributions of 2·40, 3·52 and 5·47 in the three cases: thus H^+ contributes a negative and variable refraction, depending on the deformability of the anion. If, however, the nuclear charge of the atom linked to hydrogen in a series of inert gas-like groups of the same type is progressively decreased as the number of hydrogen atoms is increased, there is a continuous increase in molecular refraction (see Vol. 1: Table XXVII and Figure LXXVI) as in the series Ne, FH, OH_2, NH_3, CH_4. This is in accordance with Section 33A above.

Following the curve from HF to CH_4 in Figure LXXVI, it is observed that increase of nuclear charge of the atom attached to hydrogen is accompanied by loss of polarity, HF being more polar than CH_4, with H_2O and NH_3 as intermediate stages. The effect of deformation is to bring the centres of positive and negative charges closer together, with consequent decrease of polar moment; when the two centres coincide, the non-polar state is reached. Fajans[23] has illustrated this with reference to the hydrogen halides. There are two limiting perfectly ideal cases: (1) the completely polar, where rigid and undeformed unlike ions are present; (2) the completely non-polar, where like atoms are associated in such a way that the centres of gravity of positive and negative electricity are coincident. The hydrogen halides then appear as intermediate between the extremes, having natural dipole moment, the dipole distances (calculated from the dipole moments divided by the electronic charge) being less than the internuclear distances, as found from the moments of inertia deduced from band spectra. The following scheme, due to Clark,[79] shows values of the dipole moments, dipole distances and internuclear distances of the four hydrogen halides. The numbers in brackets are based on estimates.

Halide	Dipole Moment μ Debye Units	Dipole Distance t Å U.	Internuclear Distance r_e Å U.	$\frac{100t}{r_e}$
HF	(1·58)	(0·331)	0·864	(38·3)
HCl	1·06	0·222	1·272	17·5
HBr	0·80	0·168	1·411	11·9
HI	0·41	0·086	(1·637)	(5·3)

If the HCl molecule had been composed of rigid ions H^+ and Cl^-, the dipole distance would have been equal to the nuclear distance, and the ratio in the last column would have been 100. If the molecule had been completely homopolar, the dipole distance and the ratio would have been zero. The actual value of the ratio lies between 100 and 0, and is 17·5; the dipole distance lies between 1·272 and 0, and is 0·222 Å.U. Thus HCl behaves as if composed of 17·5% of polar, and 82·5% of homopolar molecules, and has properties which resemble both the polar and homopolar types. It is like a homopolar body in being difficult to condense, and forming a non-conducting liquid; moreover, in the solid state, it gives a molecular lattice; it dissociates under the influence of light, and in concentrated aqueous solutions has considerable vapour pressure (10N solution has 4 mm. Hg pressure). On the other hand, hydrogen chloride resembles a polar substance in aqueous solution in behaving as a strong electrolyte, and, in dilute solutions, in giving very small partial pressures of HCl (0·1N solution has 2×10^{-6} mm. Hg). In HBr, the greater deformability of Br^- as compared with Cl^- leads to a further loss of polarity. Some further consideration of the influence of proton addition on molecular refraction is in Section 35Ba below.

The value of r_∞ for HF has been estimated as 1·000136.[79] Using this and the extrapolated experimental values of Cuthbertson[78] for the other three halides, it is possible to compare the corresponding molecular refractions with the values calculated on the assumption of additivity, the contributions being taken, from the study of organic compounds, as H 1·10, F 1·09, Cl 5·96, Br 8·86, I 13·90. The following values of $R = R_{exp.} - R_{calc}$, are then obtained: HF $2{\cdot}03 - 2{\cdot}19 = -0{\cdot}16$, HCl $6{\cdot}49 - 7{\cdot}06 = -0{\cdot}57$, HBr $8{\cdot}87 - 9{\cdot}96 = -1{\cdot}09$, HI $13{\cdot}18 - 15{\cdot}00 = -1{\cdot}82$, showing progressively increasing deviation with increasing deformability of the halogen atom.[79] This calculation is based on the assumption that the linkages between hydrogen and halogen are homopolar, as in organic compounds, and offers probably a more accurate picture of the structure of the gaseous hydrogen halide molecules than the purely electrostatic view (H^+X^-). Mulliken[80] has used the term " united-atoms " to describe these cases, whilst Clark[81] has included them in the more general group of " di-atoms."

(c) *Contrapolarization.* This term has been proposed to describe the polarization of the outer atoms of a complex ion by an anion or cation ; thus F^- may exert a deforming influence on the outer system of NH_4^+ in NH_4F.[50] Goldschmidt[82] has discussed compounds of the Type $(AX_6)B_2$ from this point of view.

35. Refraction and Physical Properties.

(A) **Refraction and Solubility.** Herzfeld and Fischer[83] showed that, especially where salts of analogous composition are compared, a salt dissolves less easily the more negative is its heat of solution. Thus NaI and AgF have positive heats of solution, whilst that of AgI (sparingly soluble) is negative. Fajans[84] pointed out that heat of solution is made up of several terms. When a solid lattice breaks up into ions, work equal to the lattice energy U must be performed ; in the subsequent process of solution and hydration of the ions, energy W is evolved, where $W = W_M + W_X$, the sum of the heats of hydration of the constituent ions. The size of W is a measure of the " hydrophile " tendency of the substance, which may still not be very soluble even when W is large unless U is relatively small. The following expression for heat of solution L is thus developed :[36]

$$L = W - U_{MX} = W_M + W_X - U_{MX} \quad \ldots\ldots \quad (5)$$

This equation is most readily applied to the comparison of a series of salts MX, M_IX, where X = Cl, Br, NO_3 . . . etc. Fajans (1928)[25] carried out the comparison for M = Ag, M_I = Na, where

$$L_{AgX} - L_{NaX} = (W_{Ag} - W_{Na}) - (U_{AgX} - U_{NaX}) \ldots (6)$$

The difference $W_{Ag} - W_{Na}$ is small and constant in these comparisons, so the differences between heats of solution are approximately measured by the differences of lattice energies of AgX, NaX. Where $U_{AgX} - U_{NaX}$ is small, as when X = F, NO_3, L_{AgX} is not very different from L_{NaX}, and similar solubility may be expected. The greater the difference $U_{AgX} - U_{NaX}$, the more negative is L_{AgX} in comparison to L_{NaX}, and the smaller the relative solubility of AgX. The values of lattice energy differences for different anions are estimated as follows :

X	F^-	NO_3^-	$\frac{1}{2}SO_4^{--}$	$\frac{1}{2}CO_3^{--}$	Cl^-	Br^-	I^-	$\frac{1}{2}O^{--}$	$\frac{1}{2}S^{--}$	$\frac{1}{2}Se^{--}$
$U_{AgX} - U_{NaX}$	9·3	10·5	11·5	17·9	25·6	31·4	39·1	45·4	49·8	63·6

In Figure LXXVII, values of the logarithms of the solubilities of salts of the type named (solubilities in molecules per 1,000 gr. water) are plotted against the differences of lattice distances.

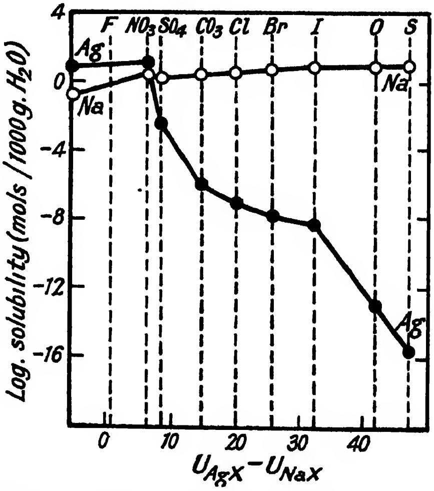


FIGURE LXXVII.—COMPARISON OF SOLUBILITIES OF CORRESPONDING SODIUM AND SILVER SALTS IN WATER.

It is observed that the fluorides and nitrates are almost equally soluble, whilst the other salts show progressively increasing differences in solubility between sodium and silver compounds in the order of increasing lattice energy differences, according to the above figures.

The estimates of the differences $U_{AgX} - U_{NaX}$ are not the same for the halides as those given in Section 33C above, but the order of sequence is the same, this being the essential point in relation to the influence of deformation. In the earlier section named, the effect of deformation upon lattice energy is discussed, and the question is further illustrated by the curves of Figure LXXVII where the superior influence of Ag^+ as a deforming cation as compared with Na^+ is clearly seen. With increasing deformability of the negative ion, and roughly in the same order, the solubilities of the silver salts fall below those of the corresponding sodium salts. The solubilities of silver compounds decrease from fluoride to iodide, and from oxide to selenide. The low solubility of AgI (wurtzite type) may be compared with those of diamond and grey tin, which are homopolar and non-conducting bodies. Yet AgI is a conductor in the solid state (see Vol. 1: 21), and hence is not a completely homopolar substance. The solubilities of the sparingly soluble silver halides are given in Vol. 1: Table XXXII.

The deformation of ions appears as an indirect factor in determining solubility, but the influence is not completely understood. It is of interest to note that whilst AgCl and AgBr are very insoluble, $HgCl_2$ and $HgBr_2$ are only moderately so, and $CuCl_2$ and $CuBr_2$ are very easily soluble. Passing from salts of Ag^+ to those of Cu^{++}, it appears that the double charge in the latter case leads to an increase of heat of hydration which exceeds the rise in lattice energy, and so there is a rise in solubility. Hg^{++} salts tend to be little dissociated, and soluble in organic solvents. In these cases, it may be supposed that one-sided deformation occurs, with liberation of deformation energy.

The influence of the hydrophile tendency of ions upon solubility is discussed by Magnus,[85] the effect being expressed in Fajans' theory by the term *W* occurring in equation (5). Thus Li^+ is small compared with other alkali metal ions, and may be expected to have considerable affinity for the water dipole. In LiF, the ions are very strongly bound in the crystal, so that, in spite of the effect mentioned, no very great solubility is to be expected for this compound. From LiF to LiI, and from LiF to CsF, the lattice energies decrease, the hydrophile tendencies also decrease as larger ions are substituted, and the solubilities tend to increase. The high solubility of AgF is associated with the highly hydrophile anion. Similar considerations apply to bivalent ions. Increasing insolubility is observed in the series $CaSO_4 \rightarrow SrSO_4 \rightarrow BaSO_4$. Here the doubly-charged ions give higher lattice energies and greater hydrophile tendencies than univalent ions. The lattice energies of the series will not be very different, so the cause of the decreasing solubility seems to lie in decreasing hydrophile tendency as the cations become larger.

Fajans' solubility rule may be expressed as follows: "For alkali halides with the same anions or cations, the solubility attains a minimum for equal heats of hydration of anions and cations, and increases with increasing difference in the heats of hydration." Linhard and Stephen[86] have studied the solubilities of 24 salts (alkali metal, silver and alkaline earth halides) in *liquid ammonia,* and find the rule to be obeyed. The influence of the dipole moment of the solvent is observed in the solubility of inorganic salts being generally less in *alcohol* than in water, alcohol having the lower dipole moment.

(B) Refraction and Ionic Dissociation. (a) *Acids and Bases.* According to a rule proposed by Kossel,[8] hydroxides give weaker bases the smaller and more highly charged the cation becomes. Thus basicity decreases in the series:

Hydroxide	$Na(OH)$	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	$PO(OH)_3$	$SO_2(OH)_2$	$ClO_3(OH)$
Charge on central Atom	I	II	III	IV	V	VI	VII

Kossel's sequence is interesting in relation to the deformation theory.[86] In NaOH, the small H^+ deforms the oxygen atom more than Na^+, and hence it comes near to the oxygen, and the substance ionizes as a base. As the charge on the central atom increases, the deformation of the oxygen by the positive cation becomes greater, tending to draw the oxygen away from H^+, and hence an increasing tendency to ionize as an acid is observed in the series.

The strengths of acids and bases run parallel with their heats of dissociation in solution, into which term the separate heats of hydration of the ions enter. In the case of acids, the same change $H^+ + H_2O = H_3O^+$ enters in, and their strengths will therefore be largely determined by the deformation of the anions. An interesting case is provided by H_2SO_4 in aqueous solution, investigated by Kohner, and discussed by Fajans, Kohner and Geffcken.[87] The curve between molecular refraction of the acid and its concentration gave a minimum at about 40 molecular per cent., which was considered to correspond approximately to the formation of a compound $H_2SO_4H_2O$ or $HSO_4^-H_3O^+$ (strictly requiring 50 mol. %). The molecular refractions are as follows: infinite dilution (extrapolated), 13·60; at the minimum, 13·45; for the pure acid (extrapolation), 13·51. The curve thus shows a rather steeper fall to the minimum on the side of lower concentration. Now the refraction of SO_4^{--} is 14·84 (Table XLIV), so the lowering of refraction due to the stabilizing of the sulphate ion by $2H^+$ in the process $SO_4^{--} + 2H^+ \rightarrow H_2SO_4$ is found to be $14{\cdot}84 - 13{\cdot}51 = 1{\cdot}33$, or 0·67 per H^+ laid on. This is equal to the estimated effect of the "destabilizing" process $H_3O^+ \rightarrow H_2O + H^+$, which should give a raising of refraction of $3{\cdot}71 - 3{\cdot}04 = 0{\cdot}67$, so that the two processes might be expected to compensate. The minimum in the curve connecting refraction and concentration finds explanation, however, in assuming that the lowering of refraction due to the laying-on of the first H^+ is greater than that due to the second H^+. Assuming that in the three changes (1) $SO_4^{--} + H^+ \rightarrow HSO_4^-$, (2) $H_3O^+ \rightarrow H_2O + H^+$, (3) $HSO_4^- + H^+ \rightarrow H_2SO_4$, the lowering of refraction associated with (1) outweighs the raising due to (2), which in turn exceeds the lowering due to (3), then the falling portion of the curve at lower concentrations may be associated with the predominance of (1) over (2), and the subsequent rise to the greater influence of (2) as compared with (3). It will be interesting to observe whether measurements on other polybasic acids lead to similar conclusions.

It will be convenient to study the effect of proton addition to molecules and ions in lowering refraction and "stabilizing" the groups. We may consider the process $I + H^+ \rightleftharpoons II$, R_I and R_{II} representing the refractions respectively before and after the proton addition. The following scheme shows estimated values of these numbers, and also $\Delta R = R_I - R_{II}$. The values of R_I for O^{--} and S^{--} are as in Section 34B, derived from comparison with inert gases by Fajans' method.[37] The values are consistent with $R_{Na^+_{soln}} = 0{\cdot}20$.

I	OH_2	NH_3	Cl^-	Br^-	I^-	OH^-	SH^-	O^{--}	S^{--}
R_I	3·75	5·63	9·07	12·66	19·21	4·76	13·28	6·95	22·7
II	OH_3^+	NH_4^+	HCl	HBr	HI	OH_2	SH_2	OH^-	SH^-
R_{II}	3·05	4·31	6·67	9·14	13·74	3·75	9·57	4·76	13·28
ΔR	0·70	1·32	2·40	3·52	5·47	1·01	3·71	2·19	9·4

It is observed that successive additions of protons to O to give OH^-, OH_2 and OH_3^+ give a decreasing sequence of ΔR's: 2·19, 1·01, 0·70. The first proton added to S$^-$ gives a diminution of 9·4, the second 3·71, in the same order. Fajans[37] studied the functions $Q_I = \Delta R/R_I$ and $Q_{II} = \Delta R/R_{II}$, and found that for OH_2 and NH_3 and the univalent negative ions exponential relations of the type $Q = a(1 - e^{bR})$, where a, b are constants, held good. A method of deriving R_I from R_{II} was thus obtained, and it was found that the R_I's of O and S^{--}, deduced from the R^{II}'s of OH^- and SH^- respectively, gave ΔR's about half as great as those given in the above scheme. It was concluded that the stabilizing influence of a doubly-charged ion was about twice as great as that of a singly-charged ion of the same polarizability.

An observation of Morelli[38] to the effect that the molecular refraction of boric acid dissolved in glycerine decreased with increasing concentration, the values being greater than for aqueous solutions of the same concentration, may be noted.

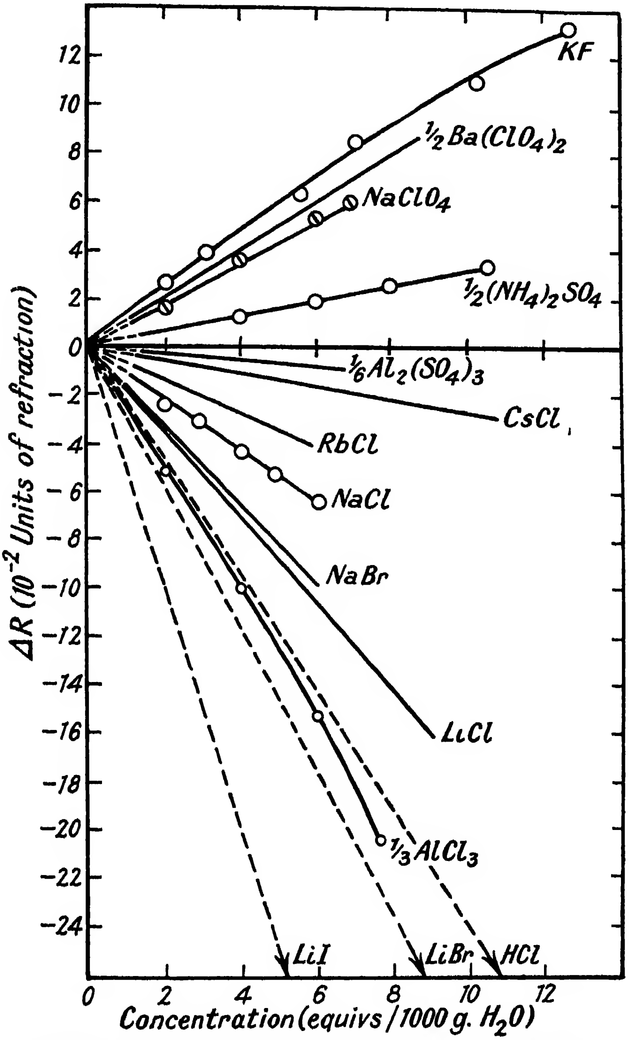


FIGURE LXXVIII.—RELATION BETWEEN MOLECULAR REFRACTION AND CONCENTRATION OF DISSOLVED SALTS (Fajans, Kohner and Geffcken).

(b) *Salts.* Figure LXXVIII, due to Fajans, Kohner and Geffcken,[87] shows the changes of molecular refraction of dissolved salts with changing concentration, and includes measurements of Huttig, Keller and Kükenthal[89] on LiBr, LiI and HCl. The curves are in all cases very approximately linear, referred to a zero limit for infinitely decreased concentration, and are based upon measurements of indices of refraction at different dilutions, and calculation of the Lorenz-Lorentz function with allowance for the refraction of the water present (subtracted). Examination of the figure shows that the salts fall roughly into three classes: (1) where the refraction increases with concentration (KF, $NaClO_4$, $Ba(ClO_4)_2$, $(NH_4)_2SO_4$); (2) where the refraction changes little with concentration (CsCl, $Al_2(SO_4)_3$); (3) where the refraction decreases with increasing concentration (RbCl, NaCl, NaBr, LiCl, $AlCl_3$, LiBr and LiI). Where the positive ion is polyvalent, the figures shown are obtained by dividing by the valency, in order to give comparable curves.

Fajans interprets the results in favour of the theory that strong electrolytes are not completely dissociated at all concentrations, an idea which has found considerable support in other directions. In order to explain the curves of Figure LXXVIII, it seems necessary to postulate that in the more concentrated solutions ions may be in immediate contact without intervening molecules of water, indicating the presence of undissociated molecules in such solutions, as Arrhenius supposed.

The three classes of curve mentioned above are found to afford very clear examples of the application of deformation principles. Assuming that the ions in solution can exert influence on water molecules in their neighbourhood, and, more especially as the concentration increases, on oppositely charged ions in contact, four possible factors may operate, as shown in Table XLV, the observed effect depending on whichever of these factors predominates in a given case.

The ΔR values of Figure LXXVII and Table XLV are referred to refraction at infinite dilution as zero, and are thus calculated from $R_{salt(c)} - R_{salt(\infty)}$, where ($c$) refers to concentration c, the values of R_{salt} being obtained by subtracting the refraction due to the water present from those obtained from measurements on solutions.

The influences (1) and (2) of Table XLV are evidently increased with increasing concentration, which brings a larger number of ions of opposite kinds into contact, according to the theory. With regard to (3), in infinite dilution, a (highly-deforming) cation lowers the refraction of water, and, as the solutions become more concentrated, this effect is reduced, by a lowering in the number of free cations. There is therefore a positive effect on the refraction of the dissolved salt, the effect becoming more marked with increasing concentration, as stated in Table XLV. (It may be remembered that the values of R_{salt} are obtained by subtracting the normal refraction of water from the corresponding values of R_{soln}, so that, according to the argument, the correction made for water is relatively too great in infinitely dilute solution as compared with the correction for concentration c, hence the values of $\Delta R_c = R_{salt(c)} - R_{salt(\infty)}$ are positive, and become increasingly so as c increases. In (4), the effect is exactly opposite to that of (3).)

TABLE XLV.—INFLUENCE FACTORS ON REFRACTION OF SALTS IN AQUEOUS SOLUTION.

Ref No	Influence	Effect	$\Delta R_{diss'd\ salt}$	Effect on ΔR of increasing concentration
(1)	Cations upon Anions	Stabilizing of Anions	Negative	Increasing negative
(2)	Anions upon Cations	Loosening of Cations	Positive	Increasing positive
(3)	Cations upon Water	Lowering of Refraction of Water	Positive	Increasing positive
(4)	Anions upon Water	Raising of Refraction of Water	Negative	Increasing negative

In comparing the refractions of ions, since the deforming force is exerted upon single electrons, the values for equal numbers of outer electrons must be used. Thus, if $R_{Cl} = 9{\cdot}0$ (8 electrons), then $R_{ClO_4^-} = 13{\cdot}32$ (32 electrons) must be divided by 4 to obtain $R_{ClO_4^-} = 3{\cdot}34$ (8 electrons), and similarly $R_{SO_4^{--}} = \frac{1}{4} \times 14{\cdot}84 = 3{\cdot}71$. In this way, the following numbers are derived for refractions of ions concerned: F^-, 2·5; ClO_4^-, 3·34; SO_4^{--}, 3·71, Cl^-, 9·0; Br^-, 12·67, I^-, 19·24; Li^+, 0·2; Na^+, 0·5; K^+, 2·23; NH_4^+, 4·13; Ba^{++}, 4·28: whilst that for water is 3·71. Referring to Figure LXXVII and Table XLV, the rising curve of KF is accounted for by Fajans as due to influence (2), the highly-deforming anion F^- operating upon the cation K^+, with a raising of refraction. (It is not clear, however, that F^- will not operate upon water, introducing influence (4), since the refraction of water given above is greater than that of K^+.) The refractions of the cations are greater than those of the anions (for equal numbers of electrons), and also greater than the refraction of water in $Ba(ClO_4)_2$, $NH_4(SO_4)_2$, so that influence (2) operates. The curve for $NaClO_4$ cannot be attributed to this cause, and must be associated with influence (3), the small highly-deforming cations operating upon water molecules and lowering their refraction, and thus increasing the apparent refraction of the dissolved salts when plotted in the way explained, the refraction of water being greater than that of ClO_4^-. The effect for $LiClO_4$ is greater than that for $NaClO_4$ in accordance with anticipation, Li^+ being smaller and more deforming than Na^+. The sulphate ions and water molecules are equally deformable, hence the influence factors (1) and (3) approximately neutralize each other in Li_2SO_4 and $Al_2(SO_4)_3$, and the curves do not show any great variation with increasing concentration. In the salts containing Cl^-, Br^- and I^-, the anions are much more deformable than water as measured by their refractions; hence the main influence factor is (1), the effect increasing as the deformabilities of the anions increase. Thus, at a given concentration, the lowering of refraction due to LiI is greater than that due to LiBr, and still greater than that due to LiCl; similar gradations are observed for NaBr and NaCl, and in the series LiCl, NaCl, RbCl and CsCl, where Li^+ is the most deforming of the four cations.

The ordinates in Figure LXXVII are expressed in 10^{-2} units of refraction, so that the changes are not very large. The result of the present discussion is to confirm the older view that undissociated molecules are present in solutions of strong electrolytes, though in a degree smaller than Arrhenius supposed.

Attention has more recently been paid to temperature as well as concentration influences. Shibata and Hölemann[90] have studied the molecular refraction of aqueous solutions of NaBr, KCl, KI, NH_4Cl and $BaCl_2$ at 25°, 35°, and 45°C. ; in each case, R falls with increasing concentration and rises with increasing temperature. In the case of $NaClO_4$,[91] R rises with rising T, and with increasing concentration, as previously observed. The same is true of Na_2CO_3,[92] but $CaCl_2$, $SrCl_2$ and $BaCl_2$ decrease linearly with concentration, the curve for $BaCl_2$ lying below that for $CaCl_2$ and $SrCl_2$, which are coincident. Geffcken and Kruis,[93] using precision methods, find that ΔR falls linearly with concentration for NH_4NO_3, whilst NaCl and KCl give maxima in about 1N solution. The results are discussed in the light of the Debye-Huckel theory of strong electrolytes. Brodsky and collaborators[94] examined TlCl, $TlNO_3$, KCl, KBr, KNO_3 and NaCl from 0·001 to 0·1N, and also investigated the temperature effect. A much steeper fall of refractivity with concentration than that found by Geffcken and Kruis was obtained for NaCl, KCl and $NaNO_3$ solutions, so that Fajans and Geffcken[95] suspected some error in the measurements.

Fajans, Hölemann and Shibita,[96] in a summarizing paper, hold that the original conceptions of Fajans and Joos have been confirmed. Additivity of ion contributions to refractivity holds for infinite dilution, the dissolved ions making different contributions from the free gas ions, as previously suggested. The effect of ions on the solvent medium is confirmed, increasing concentration leading to an increasing proportion of undissociated molecules in the solutions. The results appear in general agreement with conclusions based on the osmotic pressures of the solutions.

The temperature coefficient of molecular refraction at infinite dilution for inorganic salts may be obtained by use of the differentiated form of the Lorenz-Lorentz function :

$$\frac{\Delta R}{\Delta T} = \frac{6r}{(r^2+2)^2} \cdot \frac{M}{d} \cdot \frac{\Delta r}{\Delta T} - \frac{R}{d} \cdot \frac{\Delta d}{\Delta T} \quad \ldots\ldots\ldots\ldots (7)$$

The values for NaCl, KCl, NH_4Cl, NaBr, KBr, KI, $NaClO_4$ and $BaCl_2$ are found to be of the order 2·5 to 6·5 × $10^{\ 3}$ cm.^{3} per degree, and are greater than for the free substances, whether as solid, liquid or gas. The result is attributed to decreasing solution effect (influence of ions upon the solvent) with increasing temperature. It is necessary, in order to explain the results, to assume a small solution effect for K^+ and Cl^- and for other ions of the series, where the effect becomes still smaller (see Table XLI).

Taylor and Glover[97] have carried out studies in the refractive index of saturated aqueous solutions of $KMnO_4$.

(C) **Refraction and Absorption.** Evidence of deformation of the anions of silver salts has been given (Section 33C above) on the basis of their lattice distances and energies as compared with those of corresponding sodium salts. This is further shown by the lack of additivity of lattice distances of the silver halides,[23] and has been associated with the comparatively great deforming power of a cation not of inert gas type. Meisenheimer[98] pointed out that salts containing ions of the inert gas type were usually found to be colourless, that the chlorides of metals and hydrochlorides of organic gases were often white, whilst the iodides and hydriodides were generally coloured. The cause of the appearance of colour was found in the larger atomic volume of iodine as compared with chlorine, so that a smaller attractive force existed between the nucleus of the atom and its outer sheath in the case of iodine. This sheath of electrons was regarded as relatively unstable, so much so that the feeble energy of visible light was sufficient to displace it, with the appearance of colour. Where chlorine does not build up an ion of inert gas structure, as in Cl_2O, colour is observed.

According to the Bohr theory of atomic structure, the energy differences of an outer electron between a level and the next higher (farther from the nucleus) decrease outwards from the lowest level. The larger differences between inner levels correspond to absorption in the ultra-violet; the smaller differences between levels in the more outer region to absorption in the visible region. According to Fajans (1928)[25] deformation of anions by cations leads to a shifting of absorption from the ultra-violet into the visible region in the direction of longer waves. Thus, although Pb^{++} and I^- are colourless, PbI_2 is yellow on account of deformation: $PbCl_2$ and $PbBr_2$ are colourless on account of the smaller deformabilities of Cl^- and Br^-. A similar gradation is observed in the silver halides, where AgCl is colourless, AgBr pale yellow and AgI yellow. In the same way, development of colour in the direction of longer waves is observed in the nickel and copper halides:

NiF_2	$NiCl_2$	$NiBr_2$	NiI_2	CuF_2	$CuCl_2$	$CuBr_2$
yellowish	yellowish-brown	dark brown	black	colourless	yellowish-brown	brownish-black

According to Bohr, Ag^+, Hg^{++} and Cu^+ are symmetrical, having completed sheaths of 18 outer electrons, whilst Cu^{++} contains an incomplete sheath and readily gains an electron, so that CuI_2 is unstable and passes to CuI with liberation of iodine. Cu^{++} is apparently colourless, since anhydrous $CuSO_4$ has no colour. The familiar blue of copper salts containing water of crystallization and of the bivalent copper ion in aqueous solution may therefore be attributed to deformation of water molecules surrounding Cu^{++}.[36] Similarly, the deep blue of copper salts with co-ordinated ammonia is ascribed to deformation of ammonia molecules. It frequently happens that oxides and sulphides are coloured, whilst hydroxides and hydrosulphides are colourless, since OH^- and SH^- are stabilized by H^+, and are therefore less deformable than O^{--} and S^{--} respectively. The colour of certain substances, for example ZnO, $PbBr_2$, AgBr, is developed by heat. The greater amplitudes of heat vibrations may be supposed to bring the ions nearer together, with consequently increasing deformation. Development of colour is also noticeable in the series: $TiCl_4$ (colourless), $TiBr_4$ (pale yellow), TiI_4 (red). ThI_4 is colourless, since the thorium atom is larger and less deforming than that of titanium.

Ladenburg and Bohr linked the colour in salts of metals of group VIII of the periodic table with the presence of incomplete inner electron groups in the atoms of these metals and those adjoining them in the transition series. Fajans[25] pointed out that completion of outer electron sheaths plays no discernible part in the development of colour; thus Cu^{++} in spite of its incomplete shell is uncoloured, and Ag^+, Hg^{++} in conjunction with deformable anions lead to colour, although the sheaths of these cations are completed. It was therefore concluded that colour is no specific property of free cations, but is dependent on the anion.

Gudden and Pohl[99] discussed the relation between deformation and the photoelectric conductivities of substances. Thus many compounds where deformation is recognized to be present act as carriers in this way, for example, in the polar group, the majority of sulphides and oxides, the halides of many heavy metals and some carbonates, and, amongst the non-polar elements, diamond, sulphur, red selenium and iodine. In these non-polar substances, stabilizing of electron sheaths results in the formation of a homopolar linkage, which, according to the view of Knorr,[100] is associated with the attachment of electron orbits to more than one nucleus. It is of interest to note that these substances also act as carriers of the photoelectric current. Gudden and Pohl regard an increasing "phase-relation" between the electrons of different atoms to be characteristic of the transition from the polar to the homopolar states of matter. The effect of light on the dielectric constant of Sidot blende is noticed in this Vol.: 28B.

Ephraim and co-workers[101,102] have examined the shifting of absorption maxima of reflection spectra of the ammoniates of halides of the rare earths, praseodymium, neodymium and samarium. The addition of ammonia and water molecules causes shifts towards the violet: progressive substitution F→Cl→Br→I causes absorption increasingly towards the red end of the visible spectrum. The results are held to be in agreement with Fajans' deformation theory. thus F attracts the electrons of the rare earth ion more strongly than iodine, on account of the greater deforming power and smaller size of F. Selwood[103] has carried these observations a little farther in an investigation on the deformation of the electron shells of the neodymium ion in solutions of neodymium perchlorate.

(D) **Refraction and Dispersion.** The variation of refractive index r with wave-length λ (or frequency ν) may generally be fairly accurately represented in the case of a gas by an expression of the Sellmeier type :

$$r - 1 = \frac{a}{b - \nu^2} = \frac{a'\lambda^2}{\lambda^2 - b'} \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where a, b, a', b' are constants for the substance considered. From this, r_∞ may be found, by putting $\nu = 0$.

Dispersion of refraction may be treated similarly to refraction at a given frequency.[70] Thus, taking the frequencies of the H-β and H-α lines, it is possible to examine departure from additivity requirements by a formula $\Delta D = (R^\beta - R\alpha)_{\text{obs}} - (R_\beta - R\alpha)_{\text{calc}}$. The values of ΔD are found to follow similar rules to those outlined above for ΔR.

Recent refraction and dispersion measurements have been made on the following gases or vapours : Air,[104,113] He,[117] Ne,[117] A,[104,115,117] Kr,[115,117] Xe,[115,117] H_2,[104] O_2,[104,107] N_2,[104,105] Hg,[108,118] H_2O,[113] H_2S,[113] BCl_3,[111] BBr_3,[111] $SiCl_4$,[111] $SiBr_4$,[111] $COCl_2$,[111] CH_4,[110] C_2H_6,[111] n-C_7H_{16},[111] C_2H_2,[111] C_2H_4,[111] CH_3Cl,[110,111] CH_2Cl_2,[110,111] $CHCl_3$,[110,111] CCl_4,[110] CH_3Br,[112] CH_2Br_2,[111] CH_3CHO,[109] CH_3COCH_3,[111] $C_2H_5OC_2H_5$,[111] ; also upon HCN,[116] CH_3CN,[116] C_6H_5CN,[116] C_6H_5NC ;[116] KCl,[114] AgCl,[106] AgBr,[106] TlCl,[106] TlBr.[106] (See also [31,32,37,39,40,55,56,78].) Evidence has been obtained that liquid prussic acid consists mainly of HCN molecules.[116]

(E) **Refraction and Atomic Linkages.** The chief contributions of the deformation theory of molecular refraction to our understanding of molecular structure may be conveniently summarized under three heads.[37] (1) The influence of size, charge, departure from inert gas-like type, and (in solids) degree of co-ordination of ions have proved significant. The refraction of crystals increases with increasing co-ordination number, for example, in passing from NaCl to CsCl types. Ions not having inert gas structure are specially strongly deforming, and, in conjunction with large anions such as I , tend to set up homopolar linkages. (2) The small difference between the molecular refractions of liquid and gaseous substances may be associated with the setting up of van der Waals' polarization forces between neutral molecules. Thus for $SiCl_4$, $SnCl_4$, $SnBr_4$, CH_3COOH, $\Delta R = R_{\text{vapour}} - R_{\text{liquid}}$ is positive. (3) The increase of apparent R of 0·03 % per degree rise of temperature for dissolved electrolytes may be associated with the solution effect, or influence of ions upon the solvent. Eykmann (see [96], p. 360) found that for 40 organic liquids, between 20° and 80°C., there was a positive temperature coefficient of refraction of about 0·005 to 0·012% per degree. Measurements on changes of refraction with temperature of vapours show either inappreciable ($HgBr_2$, H_2O) or very small (CO_2) temperature coefficients, so that the results on liquids may be attributed to weakening intermolecular forces with rising temperatures. Information is thus gained on various types of forces between atoms, molecules and ions.

The deformation theory of molecular refraction has made definite contributions in the direction of clearer insight into the interactions which take place between unit particles in solids, liquids and gases. On the other hand, explanations thus far advanced have been mainly qualitative, and the theory seems to await quantitative foundation. Further, the somewhat arbitrary nature of the assignments of refraction contributions of free gas ions constitutes a weakness in the present treatment of the subject, whilst estimates are altogether lacking in the case of ions not of inert gas type. Fajans' theory none the less affords much satisfaction, and doubtless contains the germ of a fundamentally important idea. From the structural standpoint, the theory is helpful towards understanding the possible nature of molecular states intermediate between the ideal polar and homopolar types.

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(*A list of abbreviations used in references will be found on pages* xxxi *et seq*)

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CHAPTER XIII

POLAR MOLECULES

36. Measurement of Permanent Electric Moment

THE conception of atomic electric doublets was introduced by Sutherland[1] in 1895, and further extended by Reinganum,[2] Thomson[3] and Bradford.[4] The fundamentals of the theory of polar molecules, having "intrinsic" or "permanent," as opposed to "induced" moment, were due to Debye.[5] It was shown that at lower frequencies such molecules would become orientated by an applied field, and that it was necessary to introduce an orientation term into the Clausius-Mosotti expression for molecular polarization (see Chapter XI). The orientation polarization was found to vary inversely with absolute temperature, the molecular moment itself being assumed to be independent of temperature.

The order of size of dipole moment is of the electronic charge multiplied by the unit of distance; if the charge is in electrostatic (E.S.) units, and the distance in Ångströms, the magnitude will be of the order $4 \times 10^{-10} \times 10^{-8} = 4 \times 10^{-18}$, E.S.C.G.S. unit. The unit is taken as 10^{-18}, which is termed one Debye (D). All values are given in terms of this unit.

Methods available for the experimental determination of electric moment are considered in the four following subsections.

(A) **Temperature Variation Method.** Slightly modified forms of equations (8) of cap. X and (18) of cap. XI may be given as follows :—

$$PT = aT + b \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$PT = \frac{4}{3}\pi N\left(aT + \frac{\mu^2}{3k}\right) \quad \ldots\ldots\ldots\ldots \quad (2)$$

which lead to

$$a = \frac{4}{3}\pi N\alpha \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

and

$$b = \frac{4\pi N\mu^2}{9\,k} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4$$

Inserting $N = 6{\cdot}06 \times 10^{23}$ and $k = 1{\cdot}372 \times 10^{-16}$ in equation (4),

$$\mu = 0{\cdot}0127\sqrt{b} \times 10^{-18} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

If now curves are drawn from the experimental results representing the variation of PT with T, the intercepts on the PT axis will represent values of b, and the tangents of the angles of slope values of a. Figure LXIII shows the curve found by Isnardi and Gans[6] for ether, which has a polar molecule. When intrinsic electric moment is absent, $b = 0$, and the curve passes through the origin, as Isnardi and Gans found in the case of toluene. If P is plotted against $1/T$, on the other hand, the intercepts on the P axis measure a, and the tangents of slope angles give b. In this case, for $b = 0$, giving $\mu = 0$, the lines run parallel to the $1/T$ axis, as shown in Figure LXXX, CCl_4 and CH_4.

Using equation (5), Jona[7] found $\mu = 1{\cdot}53$ Debye units for NH_3 gas. Zahn[8] plotted P against $1/T$ for HCl, HBr and HI vapours, and found $\mu = 1{\cdot}03$, $0{\cdot}78$ and $0{\cdot}38$ respectively. It is noteworthy that these values are in the order opposite to that of the deformabilities of the negative ions. Zahn was able to show that by extrapolation to $1/T = 0$, that is, to high temperature, where deformability alone is operative, the polarization values decreased in the series HI to HBr to HCl (Figure LXXIX). At ordinary temperatures, the dipole effect assumes increasing importance, and the order is reversed. Sänger[9] investigated the series of liquids CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, and found $\mu = 0$, $0{\cdot}95$, $1{\cdot}59$ and $1{\cdot}97$ respectively, the moment increasing with increasing molecular disymmetry (Figure LXXX). For water, Stuart[10] found $1{\cdot}79$, and Williams[11] $1{\cdot}70$. The earlier value of Jona[7] was $1{\cdot}87 \times 10^{-18}$.

The same observer found values for SO_2 and CH_3OH of 1·76 and 1·61 respectively. Jona's curves (PT with T) are shown in Figure LXI. Equation (1) is strictly applicable only to gases, and to substances in infinitely dilute solution.

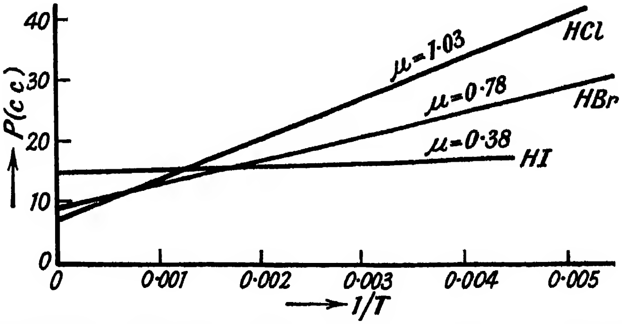


FIGURE LXXIX.—RELATION BETWEEN MOLECULAR POLARIZATION AND 1/T FOR HYDROGEN HALIDES.

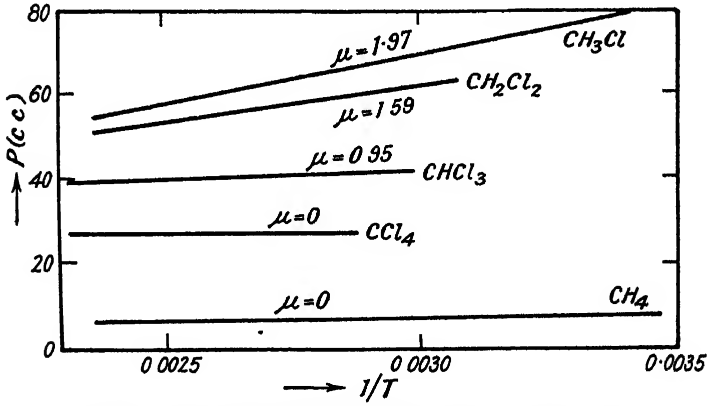


FIGURE LXXX.—RELATION BETWEEN MOLECULAR POLARIZATION AND 1/T FOR METHANE AND CHLORINATED DERIVATIVES.

(B) **Optical Frequency Method.** In this Vol. 31C, it is observed that owing to the relatively high relaxion times of molecular dipoles, the molecular refractions for optical frequencies contain no paraelectric or orientation part. Since the indices of refraction are not independent of frequency, the value R_∞ for infinitely long waves is obtained by means of a dispersion formula. If, then, $\epsilon = r^2_\infty$, the following expression independent of temperature is used :—

$$R_\infty = \frac{r^2_\infty - 1}{r^2 + 2}\frac{M}{d} = \frac{4}{3}\pi N\alpha \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

whence, using (2), it follows that

$$\mu^2 = \frac{9k}{4\pi N}(PT - R_\infty T),$$

so that, inserting values of N, k and π,

$$\mu = 0{\cdot}0127 \times 10^{-18}\sqrt{(P - R_\infty)T} \quad \ldots\ldots \quad (7)$$

from which μ may be obtained from a single determination of P at a given absolute temperature T. This method has given comparable results with the studies on temperature variation, though not always in very good agreement. For ammonia, Jona found $\mu = 1{\cdot}56$, in satisfactory agreement with the value found by the method of Section 36A above, derived from the following figures: $P = 57{\cdot}6$ c.c. at $T = 292{\cdot}2$°K; for $T = 273$°K, r (D line) $= 1{\cdot}000379$, $M/d = 22{,}400$; whence $R_\infty = 5{\cdot}7$, and $(P - R_\infty)_{292\cdot2^\circ\mathrm{K}} = 51{\cdot}9$, and the above value of μ then follows using equation (7).

(C) **Solid Dielectric Method.** Errera[12 13] suggested the use of measurements of dielectric constants of solid bodies, where the permanent dipole effect is absent, as a means of determining that part of molecular polarization which includes P_E and P_A (equation (21) of Chapter XI). Measurements on substances in the liquid or dissolved states then yield the total polarization P, whence by subtraction the orientation polarization P_0 may be found, where $P_0 = b/T$. Equation (4) then enables μ to be calculated as in the previous method (b). It was found (this Vol., 27A) that the dielectric constant of *cis*-dichloroethylene was greater than that of the trans-compound, associated with permanent moment of the *cis*-compound due to its greater lack of molecular symmetry Errera showed that the dielectric constant of the *solid cis*-compound, where the dipole effect was eliminated, was equal to that of the *trans*-compound in the ordinary state. The following values show this for the bromine and iodine derivatives :-

	$CHBr = CHBr$			$CHI = CHI$		
	t°C.	ϵ	$\Delta\epsilon$	t°C.	ϵ	$\Delta\epsilon$
cis-isomers	17 liquid	6·62	3·98	18 liquid	4·46	1·30
	−72 solid	2·64	−0·08	−30 solid	3·16	−0·03
trans-isomers	18 liquid	2·72		27 liquid	3·10	

As a result of this work, it is shown that *cis*-dichloroethylene has $\mu = 1{\cdot}89$, the *trans*-compound, $\mu = 0$, and the asymmetric isomeride $CCl_2 = CH_2$, $\mu = 1{\cdot}18$. *Ortho*- and *meta*-dichlorbenzenes have dipole moment, but not the *para*-compound.

(D) **Other Methods.** Estermann[14,15] has recently summarized the methods available for the determination of molecular electric moment. Among these, other than those mentioned above, are: the method of dipole rotation (Born and Lertes, see Vol. I: 19D), of electrostriction, of the Stark Effect in band spectra, and of the molecular ray method. It is claimed that the last-named avoids uncertainties inherent in other methods, being direct in application.[15] The experimental arrangement is similar to that used in the study of the Stern-Gerlach Effect (Vol. I: 31), but an inhomogeneous electric field is substituted for the magnetic field. Mathematical analysis was given by Kallmann and Reiche,[16] and by Stern.[17]

Early experimental work by the method of molecular rays was carried out by Clark[18] on As_2O_3, and Wrede[19] on KCl, KBr, KI and TlCl. More recently, the following dipole moments have been obtained: NaI[23] 5·10, KCl[23] 6·38, KI[23] 6·78, *quinone*[21] 0, *paranitraniline*[22] 5·6, *pentaerythritol*[20,21] 2, *pentaerythritol tetrabromide*[21] 0, *pentaerythritol tetracetate*[21] 3.

The method of determining μ's using solutions is explained in the following section. The results obtained have been discussed by Williams.[11]

37. Typical Results on Solutions

Let two components 1 and 2 be present, and let a_1, a_2 be their polarizabilities, n_1, n_2 the numbers of molecules per unit volume; M_1, M_2 the molecular weights; f_1, f_2 the fractional numbers of molecules per unit volume; P_1, P_2 the molar polarizations; P the molar polarization of the mixture and d its density. Then d is the weight of $n_1 + n_2$ molecules, so that

$$d = n_1\frac{M_1}{N} + n_2\frac{M_2}{N} = \frac{n_1M_1 + n_2M_2}{N} \quad \ldots\ldots \quad (8)$$

If, now, additivity of the Clausius-Mosotti relation is assumed,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi(n_1a_1 + n_2a_2),$$

so that, using (8),

$$\left(\frac{\epsilon - 1}{\epsilon + 2}\right)\left(\frac{n_1M_1 + n_2M_2}{d}\right) = \frac{4\pi N}{3}(n_1a_1 + n_2a_2).$$

This relation may be put in a more convenient form by using $f_1 = n_1/(n_1 + n_2)$, $f_2 = n_2/(n_1 + n_2)$, whence

$$\left(\frac{\epsilon - 1}{\epsilon + 2}\right)\left(\frac{M_1f_1 + M_2f_2}{d}\right) = P_1f_1 + P_2f_2 \quad \ldots \quad (9)$$

or

$$P = P_1f_1 + P_2f_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

A large amount of accurate work has been carried out on mixed liquids, largely by Smith,[24],[25] Williams [26] and collaborators. A few typical results will now be given, where one constituent (benzene) has negligible polar moment.

(A) **Benzene and Ethyl Ether Mixtures.** Table XLVI shows results obtained by Williams and Krchma.[26]

The table shows density and dielectric constant values for various fractional molecular concentrations represented by f_1, f_2. P is obtained from these by the use of equation (9), where $M_1 = 78$, $M_2 = 74$, and from P, values of P_1f_1 are derived, and thus of P_2f_2 by difference, using (10). The last column gives values of P_2 calculated from those of the cor-

TABLE XLVI.—MOLECULAR POLARIZATION OF BENZENE-ETHER MIXTURES

The symbols at the heads of the columns have the significance explained in the adjoining text

f_1	f_2	d_4^{25}	ϵ	P	P_1f_1	P_2f_2	P_2
Benzene	Ether	Mixtures			Benzene	Ether	Ether
1·00	0·00	0·8731	2·282	26·73 (P_1)	26·73	0·00	(54·5)
0·75	0·25	0·8297	2·713	33·73	20·05	13·68	54·7*
0·50	0·50	0·7881	3·183	40·65	13·37	27·28	54·6*
0·25	0·75	0·7465	3·691	47·52	6·68	40·84	54·5
0·00	1·00	0·7077	4·625	54·50	0·00	54·50	54·5

* Williams and Krchma give 54·5.

responding P_2f_2. It is seen that these P_2 values are practically constant.

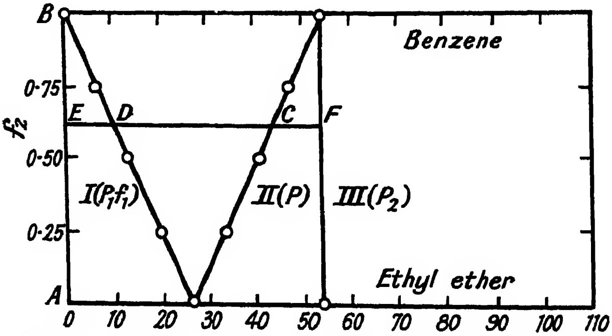


FIGURE LXXXI.—MOLECULAR POLARIZATION OF BENZENE-ETHER MIXTURES

Figure LXXXI shows the same results. Line II gives P values. An intersecting line such as CE equals CD + DE, where CD $= P_2f_2$, DE $= P_1f_1$, CE $= P$, the assumption being made that curve I, which represents the change of polarization of the benzene, is linear. Line III represents P_2 values, taken as 54·5 throughout. This curve may be obtained from the other two by CD/AE, giving EF, since AE $= f_2$, this graphical method involving the same principle as is used in calculating the values of P_2 in Table XLVI

As an example of the method, the dipole moment of ethyl ether may be calculated. First, R_∞ is found from the value of r_∞, the extrapolated index of refraction to infinite wave length. Using equation (6), Williams found $R_\infty = 23·0$, whence, inserting $P = 54·5$ in equation (7) for $T = 298°K.$, $\mu = 1·23$ (Debye units). The constancy of P_2 for ether in benzene suggests lack of molecular association of ether (see this Vol.: 40B).

(B) **Benzene and Chlorobenzene Mixtures.** A further typical case is provided by mixtures of benzene and chlorobenzene, whose dielectric constants have been determined by Smith, Morgan and Boyce,[25] and Williams and Krchma [26] Table XLVII is expressed in the same way as Table XLVI, the data being those of Williams and Krchma.

TABLE XLVII —MOLECULAR POLARIZATION OF BENZENE-CHLOROBENZENE MIXTURES

f_1	f_2	d_4^{25}	ϵ	P	P_1f_1	P_2f_2	P_2
Benzene	Chlorobenzene	Mixtures			Benzene	Chlorobenzene	
1·00	0·00	0·8731	2 280	26·73 (P_1)	26 73	0 00	(82·0)
0·90	0·10	0 8993	2·623	31·80	24 06	7·74	77·4
0·75	0·25	0·9361	3·131	38·42	20 05	18·37	73·5*
0·50	0·50	0 9946	3·979	47 71	13·37	34 34	68·7
0·00	1·00	1·1011	5 610	61·84	0·00	61·84	61·8

*Williams and Krchma give 74·5

Table XLVII provides the curves of Figure LXXXII, plotted in the same way as Figure LXXXI. The (extrapolated) value for chlorbenzene in infinite dilution is taken as 82, and used to calculate μ. Curve III is of a different type from the corresponding curve in Figure LXXXI, and shows a continuous, not linear, change of P_2 with concentration.

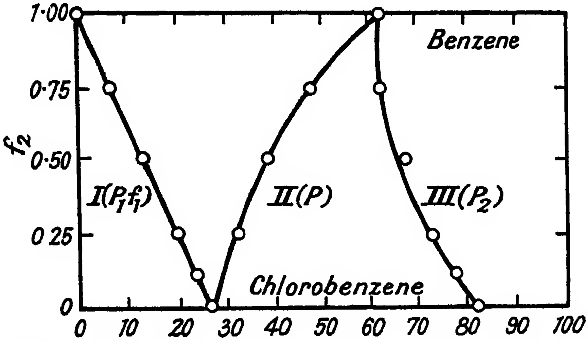


Figure LXXXII.—Molecular Polarization of Benzene-Chlorobenzene Mixtures.

(C) **Benzene-Ethyl Alcohol Mixtures.** The dielectric constants of mixtures of benzene and ethyl alcohol have been measured by Philip[27] and by King and Patrick.[28] Calculation of the polarization of alcohol at different dilutions from Philip's measurements leads to curve III of Figure LXXXIII, where a

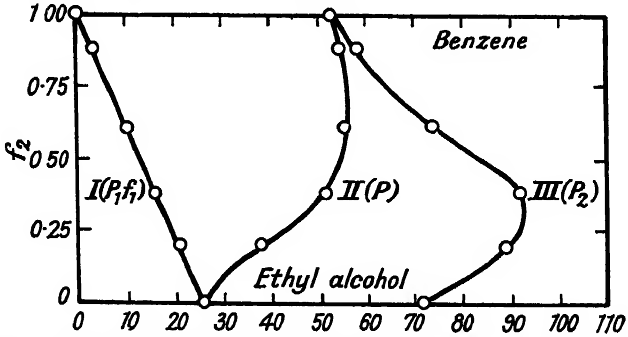


Figure LXXXIII.—Molecular Polarization of Benzene-Alcohol Mixtures.

maximum occurs at about 0·3 molecular fraction of alcohol (Table XLVIII).

Summarizing, three types of curve representing changes of polarization with concentration for a polar solute in a non-polar solvent may be recognized, where the curves are respectively (i) linear and parallel to the concentration axis (C_6H_6–$C_2H_5OC_2H_5$), (ii) not linear and without maxima or minima (C_6H_6–C_6H_5Cl), (iii) not linear with a maximum (C_6H_6–C_2H_5OH). The different behaviour of polar molecules in these respects is discussed in connection with dipoles and molecular association (this Vol.: 40B). It may be sufficient to note here the practical impossibility of formulating one mixture rule which would account for the polarizabilities of liquid mixtures in general.

TABLE XLVIII.—MOLECULAR POLARIZATION OF BENZENE-ETHYL ALCOHOL MIXTURES.

f_1	f_2	d^{16}	ϵ	P	$P_1 f_1$	$P_2 f_2$	P_2
Benzene	Alcohol	Mixtures			Benzene	Alcohol	
1·00	0·00	0·8828	2·244	25·9 (P_1)	25·9	0·0	(71·7)
0·80	0·20	—	—	38·5*	20·7*	17·8*	89·0*
0·62	0·38	0·8521	6·813	50·7	16·0	34·7	91·3
0·38	0·62	0·8396	13·09	55·4	10·0	45·4	73·1
0·14	0·86	0·81168	21·30	54·0	3·6	50·4	58·5
0·00	1·00	0·8004	27·1	51·4	0·0	51·4	51·4

* Obtained by interpolation

The procedure outlined in the present section has been extended by Williams and Allgeier[26] to the case of polar solids in benzene solution.

(D) **Solvent Influence.** Careful measurements indicate that the solvent may influence the polarization of a solute: thus, for example, phenylmethylcarbinol shows a moment of 1·55 in hexane, and of 1·60 in benzene solution.[29] The abnormal freezing-points of nitrobenzene in benzene and cyclohexane may be interpreted in terms of polarization influences [30] Ionization of a dissolved salt may prevent the extrapolation of polarization to infinite dilution.[31] Müller[32,33] has thoroughly examined the problem of solvent influence, and finds the essential effect to be connected with the dielectric constant of the solvent. The dipole moment of nitrobenzene in various solvents decreases as the dielectric constant of the solvent increases.[34] Bless[35] has observed that equation (10) neglects the internal fields of molecules, and is only strictly applicable to gases and dilute solutions. Similar views are expressed by Weigle.[36] van Arkel and Snoek[37] have proposed a modified form of equation (18) of Chapter XI, by replacing $3kT$ by $3kT + cn\mu^2$, where c is a constant and n the number of dipoles per c.c. This is applied to molecules in which one group has moment in non-associating solvents, and extended to polar solvents and associating solutes. Greene and Williams[38] have discussed cases (ethylene dichloride and dibromide in benzene, hexane and heptane) where the abnormal behaviour in solution as compared with that of the pure solute vapours is attributed to changes in the internal structure of the molecules produced by the solvent (see 38C below). Stearn and Smyth[39] suggest that results may be explained by the formation of complexes between solvent and solute (ethylene chloride in benzene and in ether). It is believed that oscillations of double bonds in the case of carbocyclic compounds containing benzene nuclei may account for variations of polarization of a given substance in different solvents.[40] Errors may also be introduced by neglecting the infra-red terms associated with atom polarization in making extrapolations to infinite wave-length from measurements made only in the visible region of the spectrum.[41,42]

38. Dipole Moments of Acyclic Organic Compounds

A complete list of dipole moments up to the date of the present work is available.[43] Attention is directed in the present and following sections to salient features of theoretical interest.

(A) **Hydrocarbons.** The dipole moment of *methane* CH_4 is zero,[43] in accordance with anticipation for a symmetrical structure. The tetrahedral symmetry of methane is supported by the study of its infra-red spectrum.[44] The C–H distance, calculated from the moment of inertia, is 1·14.[45] Boer and van Arkel,[46] assuming an ionic model $C^{++++} + 4H$, calculated the potential of the molecule, and obtained a value (181 volts) in fairly satisfactory agreement with that calculated by a thermodynamic cycle (169 volts). The model can, however, only approximately represent the true structure, which has covalent rather than electrovalent linkages. The other n-*paraffins* and the unsaturated symmetrical *ethylene* $CH_2 : CH_2$ and *acetylene* $CH \vdots CH$ molecules also have zero moment.[43] The same is true of the symmetrically substituted *dibutyl-* and *diamylacetylenes*,[47] but not of unsymmetrical *propylene*, or methylethylene $CH_3CH : CH_2$ and *α-butylene* $CH_3CH_2CH : CH_2$, or ethylethylene,[43] where μ is estimated as 0·35 and 0·37 respectively. *Isoprene*, or β-methylbutadiene $CH_2 : C(CH_3).CH : CH_2$, has practically zero moment,[43] in spite of its somewhat unsymmetrical structure. Dipole moment cannot, therefore, be the cause of the molecular association of isoprene in rubber formation. According to Farmer and Warren,[48] α substitution in butadiene $CH_2 : CH.CH : CH_2$ has a greater influence than β substitution. When $\beta\gamma$ substitution occurs, giving the symmetrical $CH_2 \cdot C(CH_3).C(CH_3) : CH_2$, neutralization takes place, giving zero resultant dipole moment.

(B) **Symmetrical Derivatives of Methane** (CR_4 Type). Normally, no dipole moment would be expected for a symmetrical tetra-substituted derivative of methane: this is fulfilled in the case of *carbon tetrachloride*, CCl_4.[43] *Tetranitromethane* $C(NO_2)_4$ in benzene solution was found by Williams to have $\mu < 0.2$, and by Weissberger 0·48.[43] It is interesting to note in this case that Mark and Noethling found a crystal structure in which one nitro-group was different from the other three (this Vol : 13B). The four groups may, however, be equivalent, even where dipole moment is found, as in *pentaerythritol* $C(CH_2OH)_4$ $\mu \sim 2$, *pentaerythritol tetracetate* $C(CH_2COOCH_3)_4$ $\mu = 2{\cdot}18$, *tetramethylmethane tetracarboxylate* $C(COOCH_3)_4$ $\mu = 2{\cdot}8$, and *tetraethylmethane tetracarboxylate* $C(COOC_2H_5)_4$ $\mu = 3{\cdot}0$.[43] Moments have also been reported for *methyl orthocarbonate* $C(OCH_3)_4$ and *ethyl orthocarbonate* $C(OC_2H_5)_4$ of 0·8 and 1·1 respectively,[49] whilst a later measurement by Fuchs[43] on the methyl compound vapour gave $\mu < 0{\cdot}3$, and probably zero. *Tetrachloro-* and *tetrabromopentaerythrite*, $C(CH_2Cl)_4$ and $C(CH_2Br)_4$ respectively, have zero moments.[43] However, a sufficient number of cases where moment is definitely present with four equal substituents has been established to require further explanation. It was first pointed out by Höjendahl[50] that if the directions of lie of the attached groups is not coincident with the tetrahedrally symmetrical valency directions of the central carbon atom, then free rotation and interaction may give rise to moment. This explanation was adopted by Williams,[51] and is now accepted, in preference to an earlier suggestion of Weissenberg,[52] who thought a pyramidal structure with the four groups in a plane, the carbon atom being at the apex, might account for the anomaly. In the course of his work on expanded films on aqueous surfaces, Adam has found independent evidence of tetrahedral symmetry in the case of *pentaerythritol tetrapalmitate* (see literature cited in Vol. 1: 33Ca).

(C) **Compounds containing Halogens.** The moments recorded by different observers sometimes vary fairly considerably, especially when measurements are made in solution. The direct measurements on gases and vapours may generally be presumed to be most accurate. In what follows, the apparently most probable numbers are chosen.

The results for the halogenated methanes may be tabulated as follows.[43]

X	F	Cl	Br	I
CH_3X	1·81[53,57]	1·85	1·80	1·64
CH_2X_2	.....	1·50	1·39	1 08
CHX_3	.. ..	1·05	0·99	0 80

The values decrease in the series chlorides→bromides→iodides, also from chloride→fluoride and from $X \to X_2 \to X_3$ derivatives. The relatively low value of CH_3F may perhaps be due to deformation of the CH_3 group by the F atom, with consequent lowering of the dipole distance.[53] In the X_2 and X_3 compounds, repulsive forces between the halogen atoms distort the tetrahedral structure, and thus reduce the moment.[54] The angles between the chlorine valency directions are found to be 124° for CH_2Cl_2, and 116° for $CHCl_3$,[55,56] in agreement with the X-ray measurements of Bewilogua.[107] The fall from chlorides to iodides may possibly be associated with increasing polarizability of the halogen atom.[57]

The following table compares members of homologous series :—

	X→	F	Cl	Br	I
Methyl	CH_3X	1·81[57]	1·85	1·80	1·64
Ethyl	CH_3CH_2X	1·92[57]	2·03	1·79	1·62
n-Propyl	$CH_3CH_2CH_2X$	......	2·04	1·94	1·63
Isopropyl	$(CH_3)_2CHX$	......	2·04	2·09	1·99
n-Butyl	$CH_3CH_2CH_2CH_2X$	......	1·97	1·97	1·88
Isobutyl	$(CH_3)_2CHCH_2X$	......	1·96	1·97	1·87
Secondary butyl	$CH_3CH_2CH(CH_3)X$	......	2·09	2·12	2·04
Tertiary butyl	$(CH_3)_3CX$	......	2·15	2·21	2·13

Comparing normal paraffins, there is no appreciable increase in dipole moment with increasing chain length, except possibly from methyl to ethyl in the fluoride and bromide series.[54,57,58] The observed moment is mainly to be associated with the C–X linkage ; induction from this part of a molecule may raise the moment from MeX to EtX, but has no influence past the second C atom from it.[54] Polarization effects are also operative.[57] An exact quantitative consideration of the influence of a dipole on the remainder of a molecule containing it is at present impossible, though various qualitative suggestions have been made [53] Since the experimental numbers are often considerably divergent, and the theory is insufficiently developed, it appears undesirable to pursue this matter from the quantitative standpoint at the present stage.

It is interesting to compare the variations with structure in the butyl halide isomerides, discovered by Parts [59] The above table shows that the moments increase in the series normal→ secondary→tertiary halides, whilst the normal and iso- varieties have approximately equal values. This finds a simple interpretation in terms of structural considerations.[60] If only two carbon atoms distant from the principal dipole are affected by induction, then in the secondary compound three, and in the tertiary compound four carbon atoms are affected. Since the branching in the chain in the iso-isomer occurs at the carbon atom two distant from the dipole centre at the C–X linkage, it may be expected that normal and iso-compounds will have approximately the same moment

van Arkel and Snoek[108] have found that boiling-point data give evidence of dipole moments in the case of halogenated methanes. Of two isomers, the lower boiling tends to have the higher moment. The moment introduced by an F atom is comparable with that due to Cl or Br: thus CBr_2F_2 and CBr_3F have zero moments.

Gross[61] has considered the series: CH_2Cl_2 $\mu = 1{\cdot}50$, $CHCl_2CH_3$ 1·98, $CHCl_2CH_2CH_3$ 2·06, $CH_3CCl_2CH_3$ 2·18, where substitution of H by CH_3 causes an increase in moment. It is considered that an induced moment in the CH_3 group must be regarded as unlikely, and the results are attributed to polarization effects, acting in such a way that the angle between the C–Cl dipoles will be less, and therefore the moment larger, in $CHCl_2CH_3$ than in CH_2Cl_2, since in the former case only one H atom is attached to the C atom carrying the dipoles. Similar explanations are extended to other cases. It becomes clear that induction alone is insufficient to explain all the observations, and that other influences must be taken into account.

Müller and Sack[62] have investigated 1·2 trans-*dichloroethylene* and 1·2 cis-*dichloroethylene* CHCl : CHCl, and find moments of $<0{\cdot}70$ and 1·74 respectively. Probably the trans-compound has zero moment, as Errera[63] found for the corresponding Cl–Br, Br–Br and I–I compounds. The effect of the doublets is reinforced in the cis-compounds. As the sizes of the substituent halogen atoms increase, so the angle between them is widened, with corresponding diminution of moment. For the Cl–I compound CHCl : CHI, however, the order is reversed: cis $\mu = 0{\cdot}57$, trans 1·27. It is supposed that the I atom carries a positive charge relative to the Cl atom, so that the moments cancel more nearly in the cis-compound where the dipole groups are nearer together. Stuart[64] finds the cis-forms of these compounds to be the more stable.

A large amount of work has been carried out on compounds of the type CH_2XCH_2X, where the interesting phenomenon of a variation of dipole moment with temperature has been observed, in disagreement with expectation on the grounds of the earlier Debye theory. The dipole moment of *ethylene dichloride* (dichloroethane) CH_2ClCH_2Cl was determined by Ghosh, Mahanti and Sen Gupta[65] as 1·57, and originally believed to be independent of temperature. Williams[66] found that for a molecule of this type, assuming free rotation about the C–C bond, so that any orientation of the two dipole bonds C–Cl was equally likely, the dipole moment was given by $\mu = \sqrt{2}m.\sin\theta$, where m is the moment of each C–Cl linkage, and θ the angle of inclination of the C–Cl dipoles with the central C–C direction. The value of m was taken as 2·0, equal to the current value for CH_3Cl. This gave $\theta = 38°$, as compared with the tetrahedral angle 70°, so that considerable repulsion of the polar groups was assumed, leading to departure from the normal tetrahedral symmetry of carbon bonds. Meyer[67] investigated the molecular model more closely, and found that if the intramolecular potential, due to interaction between the polar groups, exceeded a certain critical amount ($0{\cdot}1kT$) free rotation of the C–C bond would be hindered. He therefore said that the dipole moment of ethylene dichloride should increase with temperature, since rising temperature would gradually weaken the interaction of the groups and thus favour free rotation. The variation with temperature was experimentally established by Zahn,[68] who found that the moment was 1·12 at 32°C. and 1·54 at 270°C. Sänger[69] argued in favour of Williams' view of free rotation, to which Meyer[70] replied. Smyth and Kamerling[71] extended the argument to *ethylene dibromide* CH_2BrCH_2Br, and to polymethylenes of the type $Br(CH_2)_nBr$, where $n = 3, 5$ and 10. For the case $n = 10$, no variation of moment with temperature was found, indicating that the active groups were too far apart to influence each other, and that there was no pronounced bending of the hydrocarbon chain. Long chains with independent dipole groups at their ends have a moment given by $\mu = \sqrt{2}m$, where m is the group moment associated with either dipole linkage.[72] Ethylene bromide shows a higher moment in benzene than in heptane at the same temperature, the benzene for some reason weakening the force between the dipole links.[73] An extension of Meyer's calculation showed results in agreement with classical and wave mechanics.[74] Mizushima and Higasi[75] adopted the theory of lack of free rotation in interpretation of the variation of moment of ethylene dichloride with temperature, whilst Greene and Williams[76] admitted that the assumption of free rotation was unjustified, since mutual repulsion between the dipole groups would not cause so large a deviation from the tetrahedral model as that originally found by Williams. An undeformed tetrahedral angle between the C–C and C–Cl was assumed (70°), and the contributions C–Cl and C–Br were found to be 1·46 and 1·20 respectively. Lennard-Jones and Pike[77] have given mathematical treatment to the cis- and trans- models of ethylene dichloride. Smyth and Walls[109] have considered the calculation of dipole moments in aliphatic chains of varying length, when 2, 3 or 4 dipoles which may move relatively to each other are present, following the method suggested by Eyring.[110] Zahn[111] has also considered the constitution of molecules having several axes of free rotation in the light of dipole moment measurements. No noticeable dependence on temperature was observed in the cases of *ethylene chlorhydrin, ethylene glycol, ethylene diamine* and *succinic acid diethyl ester.* Zahn[78] has conveniently summarized the position concerning this interesting theory, in a paper to which further reference may be made.

The equation suggested by Williams[65] mentioned above, applicable to the case of symmetrical molecules of the type CH_2XCH_2X, for free rotation about the C–C bond, turns out to be a special case of the equations of Eyring[110] and Meyer[67] deduced for hindered rotation due to interaction of the two dipole groups X. Thus Eyring's equation reduces to that of Williams for the case of free rotation about a single bond, whilst Meyer's relation takes the same form at high temperatures, at which the rotation becomes free.

The conception of lack of free rotation in ethylene dichloride is foreign to the classical interpretation of the single C–C linkage. There is, however, no necessary discordance, for the linkage considered is free as compared with that in dichloroethylene, for example, but the rotation is hindered to some extent by the interaction of the polar groups. The possibility of the presence of mixed states must also not be overlooked: a mixture of molecules of two kinds, one permitting and the other inhibiting free rotation, would lead to the observed behaviour.

The general question of the possible additivity of contributions of group moments to molecules as a whole is considered in Section 39A.

(D) **Alcohols, Mercaptans, Ethers and Thioethers.** The most probable moments taken from the tables[43] are as shown on page 348.

This group of substances forms triangular molecules like those of water and hydrogen sulphide. The angle between the oxygen valency directions is probably about 115° and between the sulphur valencies about 90°, and these angles may not vary very much in different compounds.[79] A further important fact emerges from the table overleaf, that the moments in a given series of compounds are practically independent of chain

Alkyl Group R		ROH	RSH	ROR	RSR
Methyl	CH_3-	1·68	......	1·29	1·40
Ethyl	CH_3CH_2-	1·69	1·39	1·15	1·58
n-Propyl	$CH_3CH_2CH_2-$	1 66	1·33	1·16	1 55
Isopropyl	$(CH_3)_2CH-$	1·70	......	..	. ..
n-Butyl	$CH_3CH_2CH_2CH_2-$	1·66	1 40	...	1 57
Isobutyl	$(CH_3)_2CHCH_2-$	......	...	.	1 58
2-Butyl	$CH_2CH_2CH(CH_3)-$	1·75	. ..	.	.. .
3-Butyl	$(CH_3)_3C-$	1·67	. ..		. .
n-Amyl	$CH_3CH_2CH_2CH_2CH_2-$	... .	1 51	..	1·59

length. The absence of an inductive effect in the series of alcohols may be associated with localization of the moment in the neighbourhood of O atoms, the resultant being determined by combination of C–O and O–H moments.[80] The moments agree with Debye's equation for variation of dielectric constant with temperature at higher temperatures where association is absent.[81] The constancy of moment in the homologous series of alcohols is further shown by measurements on the higher members by Ghosh, Sack and Higasi.[43] Ethyl mercaptan has a higher dipole moment than hydrogen sulphide ($\mu = 1{\cdot}0$), which Hunter and Partington[82] have suggested may be due to induction. If this is so, one would expect a lower moment for methyl than for ethyl mercaptan, but no measurements are available to check this point, although a definite increase seems to appear between methyl and ethyl thioethers. It is noteworthy that the thioethers have greater moments than the corresponding ethers, whilst the mercaptans have lower moments than the alcohols. It appears that the group moment C–S is greater than that of H–S, whilst between C–O and H–O the order is reversed.[83,84]

Smyth and Walls[85] have examined four glycols of the general formula $OH(CH_3)_nOH$, obtaining the following moments: $n = 2$ (ethylene glycol), 2·30; 3, 2·51; 6, 2·48; 10, 2·54. The compound $CH_3CHOH.CH_2OH$ gave $\mu = 2{\cdot}28$. No sensible variation of moment with temperature was detected, and free rotation around the C–C bonds must therefore be assumed.

It may further be presumed that no pronounced bending of the chains takes place.

(E) **Acids and Esters.** The moments for the following aliphatic acids and esters are approximately as follows :—[43]

X	XCOOH	$(XCOOH)_2$	HCOOX	CH_3COOX	C_2H_5COOX	C_3H_7COOX
H	2·07[86]	0·99		1·73	1·73	0·78
CH_3	1·73	1·04		1·76	1·71	1·74
C_2H_5	1·73	0·88	1·92	1·81	1·77	1·78
n-C_3H_7	0·78	0·93	.	1·85	1·80	1·97
n-C_4H_9	0·63*	0·89*		1·87	1·81	

* Isovaleric acid

Zahn[87] measured the moments of formic, acetic and propionic acids, and found a variation with temperature, which was explained as due to changing degree of association. Above the temperatures at which only single molecules were present, the moment was found to be unaffected by temperature. This might be interpreted in favour of free rotation about the single bonds, but Meyer[67] found that a temperature of 20,000°C. would be necessary to yield free rotation, so that one would not expect to find any appreciable variation in moment on this account working at temperatures available in the laboratory. After the first three members of the fatty acid series, the moment becomes constant in the neighbourhood of 0·7 (see measurements on palmitic and myristic acids[88]). Wilson and Wenzke[86] found the moments of single molecules of the first three members in dioxane solution. Earlier work in benzene solution referred to double molecules $(XCOOH)_2$, since association is well known to occur in this solvent. The moments of acetic and propionic acids in hexane solution were found by Piekara[89] to vary with temperature, a result which the author regarded as partly due to association, in agreement with the earlier conclusion of Zahn.

Smyth and Walls[90] adopted a model of the carboxyl group in which the H^+ was attracted to the O^- of the carbonyl group, and argued that Zahn's observation of temperature variation in the case of acetic acid might be due to hindrance of free rotation in the C–OH linkage, as in the case of ethylene dichloride discussed above. Zahn found that the moment became constant above about 200°C., so that if Meyer's calculation of the high temperature necessary to bring about free rotation is accepted, it is clear that the experimental variation below 200°C. cannot be associated with increasing freedom of rotation in this region of temperature. Two independent causes may bring about variation of moment with temperature : lack of free rotation due to interaction of dipole groups, and association varying with temperature. Zahn's result is probably correctly interpreted as due to the latter.

Wolf and Gross[91] suggested that the moments in homologous series should be found to alternate with odd and even numbers of C atoms, as is the case with melting-points and other constants (Vol. I : 14 ; this Vol. : 13F). It appears impossible to maintain that this alternation exists for dipole moments, for, as already noted, the values are constant within the limits of experimental error in a series, excepting where other causes, such as inductive influences, are operative. Müller and Sack[02] observed constancy in the series of esters of acetic acid.

Cuy[92] suggested that in hydrocarbon and other aliphatic chains the carbon atoms were charged alternately positively and negatively, and Smyth[93] discussed the electric moments of acyclic compounds from this point of view, and found that no evidence of measurable alternation was available. The conception of alternating polarities is open to much criticism, and Carothers[94] and Kharasch and Darkis[95] have found that the observed alternation of physical properties in homologous series (melting-points, heats of combustion, etc.) affords no proof of intramolecular alternation of polarity. Convincing proof of this contention is found in the lack of alternation of dipole moment in series of corresponding compounds. The behaviour of other physical constants in series can be interpreted in terms of a zig-zag arrangement of the carbon chains (this Vol. : 13).

The esters show no appreciable temperature variation of moment.[96] It seems probable that free rotation is possible in these cases, since the alkyl group substituted for H^+ in the carboxyl group would not be expected to undergo much interaction with the carbonyl oxygen atom.

Compounds of the type $COOC_2H_5(CH_2)_nCOOC_2H_5$ show no appreciable change of moment as n is increased from 0 to 8 to 18.[90] The long chains have presumably extended structure, which do not bend appreciably in weak external fields, so that their end dipoles cannot interact.

Aliphatic amino-acids and polypeptides, containing the $NH_3^+CH_3COO^-$ "zwitterion" in solution, show regularly-increasing dipole moments as the number of C atoms between the poles increases.[97] The measurements enable calculations of the distances separating the polar groups to be made.

Weissberger and Sängewald[98] found that polymorphic forms of *dimethyl tartrate* give equal moments, and that no evidence of compound formation on racemization can be found in the case of *dimethyl mandelate*, the *d* and *dl* forms having the same dipole moment.

(F) **Compounds containing Nitrogen.** The approximate moments of some simpler compounds of this class may be given as follows :—[43]

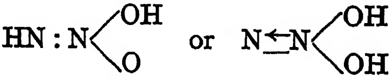
		$—NH_2$	$—NO_2$ (nitro-)	$—NO_2$ (nitrite)	$—NO_3$	—CN	—SCN	—NCS (iso-)
Methyl	$CH_3—$	0·99	3·02	.	2·85	3·16	3·56	3·18
Ethyl	$CH_3CH_2—$	0·99	3·19	2·38[99]	2·91	3·66	3·64	3·31
Allyl	$CH_2:CHCH_2—$	1·20	. .		. .	.. ..	. .	3·30
n-Propyl	$CH_3CH_2CH_2—$	1·39	.	2·28	2·98	3·46	. .	. .
Phenyl	$C_6H_5—$	1·52	3·73	.. ..	. . .	3·90	3·59	3·00

Werner[100] considered that length of chain had no influence on the dipole moments of amines, but this is not borne out by the above numbers. There is apparently no change between methylamine and ethylamine, but an increase seems to occur later in the series, so that the analogy envisaged by Werner between amines and alcohols is not complete. The resemblance between the methyl and ethyl compounds is also found in the secondary and tertiary amines: the moments decrease in the order primary→secondary→tertiary compounds.[101] The nitro-group seems to show appreciable induction, as is evidenced by the increase in moment from nitromethane to nitro*n*-butane ($\mu = 3{\cdot}29$).[102] On the other hand, the moments in the series of alkyl nitrates are very nearly constant (*n*-butyl nitrate has $\mu = 2{\cdot}96$), so Cowley and Partington[103] suggested that, if the valency angle of —O— is 90°, the NO_2 group in the nitrates lies with its dipole axis at right angles to the hydrocarbon chain, and its resolved inductive effect will be therefore zero. Smyth and McAlpine[104] find that the vapour molecule of nitromethane has a dipole moment consistent with the tetrahedral carbon model. The value 3·42, higher than appears in the above table, is found.

Appreciable induction is seen in the series of cyanides[100] and isothiocyanates,[105] but not of normal thiocyanates[105] (see table above). Hunter and Partington deduce that the isothiocyanate chain has a linear structure, of the form $C^+{-}N^- = C^+ = S^-$. Direct addition of the moments attributed to the three linkages in the order shown gives $\mu = 0{\cdot}6 + 3{\cdot}4 - 1{\cdot}2 = 2{\cdot}8$, which is only slightly less than the observed moment of methyl isothiocyanate The normal thiocyanates are assigned another structure, with the –SCN dipole direction inclined at an angle of 120° to the C(hydrocarbon)–S link.

Fogelberg and Williams[106] have studied binary liquid mixtures of amines, with a view to throwing light on the stereochemistry of nitrogen. The observations are consistent with the generally-accepted pyramidal model of the valency directions in ammonia (this Vol.: 42H).

Hyponitrous acid[102] is assigned the *trans*-structure, HO.N : N.OH. *Nitroamine*, NH_2NO_2, may have either of the formulæ



$$HN : N \begin{matrix} \diagup OH \\ \diagdown O \end{matrix} \quad \text{or} \quad N \overset{\leftarrow}{\underline{\quad}} N \begin{matrix} \diagup OH \\ \diagdown OH \end{matrix}$$

(G) **Triglyceride Oils.** Bless[112] found the dipole moment of *tung oil* to be 2·29, and concluded that clusters were present in the liquid similar to Stewart's cybotactic groups. (Tung oil consists of 80–85% of trielæostearin and 15–20% triolein.) Stoops[113] found μ = 2·8 for tung oil, 3·0 for *linseed oil* (trilinolin), 3·7 for *castor oil* (triricinolein) and 2·7 for *tristearin.* In the group of triglyceride oils, therefore, the dipole moments lie between about 2·5 and 3·5, and there is considerable interaction between the dipole groups (*e.g.*, OH) in neighbouring long chains.

39. Dipole Moments of Cyclic Organic Compounds

(A) **Carbocyclic Division.** (a) *Group and Link Moments.* A certain measure of success has attended the treatment of dipole moments of groups within molecules as vectorially additive quantities, whereby the moments of molecules may be calculated and compared with experiment. It is convenient to discuss this in connection with cyclic compounds, since it is largely to these that the method has been applied. Some light has also been thrown on the angles between linkages in molecules.

An extension, admittedly more doubtful, has been made in assigning moments to individual linkages in molecules. Although the empirical methods employed are sometimes reasonably effective in the calculation of molecular moments, the number of assumptions which it is necessary to make in deriving link moments tends to lessen the value of this procedure. It is noteworthy, therefore, that Allard[114] justifies the vectorial addition of link moments by wave mechanics.

Considering group moments, Höjendahl[50] pointed out tha since the dipole moment of an homologous series of compounds approaches constancy, each group may be assigned a characteristic moment which can be treated as a vector. In general, it has been found necessary to assign a different value for a given group, according as it takes part in a long chain or benzene ring compound. In the latter case, the benzene ring is assumed to make zero contribution, and the assignment to an aromatic group R may be taken as equal to the moment of the compound C_6H_5R. The following values are based upon estimates quoted by Sutton,[56] Wolf[116] and Bruyne, Miss Davis and Gross,[117] the numbers given in brackets referring to chain (aliphatic) compounds, and those without brackets to benzene ring (aromatic) compounds :—CH_3 (0) +0·45 ; Cl (−2·15) −1·56 ; Br (−2·21) −1·52 ; I (−2·13) −1·27 ; =O (−1·29) −1·06 ; CH_2Cl (−2·03) −1·82 ; $CHCl_2$ (−2·06) −2·03 ; CCl_3 (−1·57) −2·07 ; OH −1·7 , CHO −2·8 ; OCH_3 −1·2 ; COOH −0·9 ; $COCH_3$ (−2·79) −2·97 ; CO (−2·76) −3·04 ; CN (−3·46) −3·90 ; NC −3·6 ; NO_2 (−3·05) −3·94 ; NH_2 (+1·23) +1·55. Amongst these groups, CH_3 and NH_2 are reckoned positively, all the others negatively. Sutton[115] pointed out that the difference between μ (aromatic) and μ (aliphatic) is positive in sign for CH_3, NH_2, : O, Cl, Br, I and CH_2Cl, which are known to favour ortho- and para-substitution in di-derivatives. These groups, therefore, are held to cause electron shifts away from them towards the benzene ring. Other groups, CCl_3, $COCH_3$, CO, CN and NO_2, give negative values of the above-named difference, and are meta-directing in di-derivatives, indicating an electron shift towards the groups away from the benzene ring. Thus considerable light is shown on the inductive influences of groups upon the benzene ring by comparison with their behaviour in aliphatic compounds.

The suggestion that the extension might be made to linkages was due to Eucken and Meyer.[118] Apart from difficulties inherent in the underlying assumptions (mentioned above), it appears that it may be necessary to assign somewhat different contributions to links according as one or other of the atoms concerned in forming a link are singly, doubly or trebly linked to other atoms. Although Smyth and Dornte[119] thought that no moment need be attached to the double bond in ethylene, others, notably Allard[120] and Wilson and Wenzke,[121] have found it necessary to make allowance for the presence of unsaturation. Since, however, the method is at best no more than an empirical approximation, these corrections need not concern us deeply. Instead, it will be convenient to quote the following assigned link moments (taken mainly from Eucken and Meyer[118] and Malone[122]) : C–C = 0 ; C–O (ketones) 2·3 ; C–O (ethers) 0·7 ; C–H (0·4) 0 ; C–Cl 1·56 ; C–Br 1·49 ; C–I

1·30; C–N 0·6; C–Me 0·4; H–O 1·6, 1·32; H–S 0·93, 0·63; Me–S 1·40; Et–S 1·57; Ph–S 2·24; H–Cl 1·03; H–Br 0·78; H–I 0·38, H–N 1·04; H–P 0·36; H–As 0·10. To these may now be added the estimated H–F 1·58.[123]

An example of Eucken and Meyer's procedure is as follows. The molecule of *methyl alcohol* CH_3OH is assumed bent at the oxygen atom, the OH group making an angle of 110° with the OCH_3 line. We have therefore to add vectorially (a) a moment of 1·6, associated with O–H, and (b) the moment due to the remainder of the molecule = (O–C) + (C–Me) = 0·7 + 0·4 = 1·1, (a) and (b) being set at 110°, the angle of the HOH molecule. We can add these vectors by the formula $\mu^2 = \mu_a^2 + \mu_b^2 - 2\mu_a\mu_b\cos\theta$, or, more simply perhaps, draw two lines of lengths 1·6 and 1·1 inclined at 110°, complete the parallelogram, and measure the diagonal resultant. In this way, 1·55 is obtained for the final moment, as compared with experiment 1·68. Close agreement between theory and experiment was also obtained for certain di-derivatives of benzene. In other cases to which the method has been applied, the agreement is not so good. For example, Zahn[124] found that calculation gave 2·28 for *acetyl chloride*, as against the experimental result 2·68.

A general summary of applications of dipole moments to chemical problems has been given by Debye.[125]

(b) *Substituted Derivatives of Methane.* Two equal moments μ' inclined at an angle θ combine to give a resultant along the bisector of the angle $\mu = \mu'\sqrt{2(1 + \cos\theta)}$ (see cap. XIV, Appendix: 6). This was applied by Bergmann and co-workers[55] to *methylene chloride* CH_2Cl_2. The two C–H vectors of $\mu' = 0·4$ set at the tetrahedral angle 109° combine, by the above formula, to give $\mu_{CH_2} = 0·46$. The measured moment of CH_2Cl_2 being taken as 1·54, the resultant moment due to the two Cl vectors is $\mu = 1·54 - 0·46 = 1·08$. Taking μ' (Cl) = 1·56, the angle between the Cl's should be θ given by $1·08 = 1·56\sqrt{2(1 + \cos\theta)}$, which yields $\theta = 139·5°$. This does not agree with Bewilogua's measurement using X-rays of 124 ± 6°.[107] Hampson and Sutton[126] obtained 131 ± 3°, a more concordant result.

The angles in *di-phenyl substituted methanes* having Br or NO$_2$ in para-positions to the CH$_2$ group are found as follows.[55] The experimental moment of $(C_6H_5)_2CH_2$ being 0·3, and that of $(p.\text{–}BrC_6H_4)_2CH_2$ 1·79, the moment due to the Br atoms is $1{\cdot}79 - 0{\cdot}3 = 1{\cdot}76$. Taking the group moment of Br as 1·49, we have $1{\cdot}76 = 1{\cdot}49\sqrt{2(1 + \cos\theta)}$, giving $\theta = 120°$. A similar calculation for the corresponding nitro-compound by the expression $4{\cdot}29 - 0{\cdot}3 = 3{\cdot}98\sqrt{2(1 + \cos\theta)}$ again yields $\theta = 120°$, from which good agreement is obtained with the experimental angle 124° for CH_2Cl_2.

Three equal vectors μ' acting along the edges of a triangular pyramid combine to give the resultant $\mu = \mu'\sqrt{3(1 + 2\cos\theta)}$, where θ is the angle between any pair of vectors (see cap. XIV. Appendix: 7). Bergmann[55] used this relation in connection with tri-substituted derivatives of methane CXY_3. The measured moment of $CHCl_3$ being taken as 1·23, the resultant of 3 Cl's is estimated as $1{\cdot}23 - 0{\cdot}40 = 0{\cdot}83$, whence $0{\cdot}83 = 1{\cdot}56\sqrt{3(1 + 2\cos\theta)}$, giving $\theta = 117°$, in agreement with Bewilogua's measured 116 ± 3°. Hampson and Sutton[126] obtained 116° 16′ ± 10°. The error in making these estimates is thus considerable.

The moment of *triphenylmethane* $(C_6H_5)_3CH$ is 0·62, and of *trip-nitrophenylmethane* $(C_6H_4NO_2)_3CH$ 3·23, whence the effective moment of the three nitro-groups may be taken as $3{\cdot}23 - 0{\cdot}62 = 2{\cdot}61$.[55] The angle between these groups may then be estimated by means of $2{\cdot}61 = 3{\cdot}98\sqrt{3(1 + 2\cos\theta)}$, where 3·98 is the group moment of NO_2. This yields $\theta = 116°$, in agreement with the $CHCl_3$ angle. A similar calculation applied to *triphenylchlormethane* $(C_6H_5)_3CCl$ ($\mu = 1{\cdot}93$) gives the angle between the phenyl-group valency directions as $\theta = 109°$.[115] The corresponding di-derivative *benzophenone-chloride* $(C_6H_5)_2CCl_2$ ($\mu = 2{\cdot}39$) yields $\theta = 106°$ between the valency directions of the phenyls, whence it is concluded that C_6H_5 and Cl have approximately equal space requirements.

(c) *Compounds containing One Benzene Ring.* (i) *Benzene and its Monoderivatives.* In spite of early suggestions that benzene possesses a finite dipole moment, the results of more recent investigations show the moment to be zero,[127,128,129] in accordance with anticipation for a symmetrical structure. Accepting this, the group moments in aromatic compounds are often taken as equal to those of the mono-substituted benzene derivatives containing the group in question. *Toluene*[127] has a small moment, about 0·4, apparently attributable to induction influences by the methyl group. Recent measurements[129] on *chlorobenzene*, *nitrobenzene* and *phenyl cyanide* have yielded the moments 1·69, 4·23 and 4·39 respectively, values rather higher than have been previously reported. The moments of *fluorobenzene* (1·45) and *bromobenzene* (1·49) appear rather less than that of chlorobenzene, whilst *iodobenzene* has the smallest moment in the group of compounds (1·30).[43] The same progression has been noticed among methyl halides (this Vol.: 38C). Parts[130] has studied the series *benzyl chloride* $C_6H_5CH_2Cl$, *benzal chloride* $C_6H_5CHCl_2$ and *benzotrichloride* $C_6H_5CCl_3$, finding the moments 1·85, 2·05 and 2·15 respectively. These figures may be compared with CH_3Cl 1·85, CH_2Cl_2 1·50 and $CHCl_3$ 1·05, where the sequence decreases within creasing number of Cl atoms. The relationships between the two sets of compounds do not appear to be very clear. Parts finds that benzyl chloride has an approximately tetrahedral structure, whilst the di- and tri-chlorderivatives have valency angles smaller than the tetrahedral requirement, the deviation being attributed to the presence of the phenyl group. In other cases, replacement of H by C_6H_5 may not affect the moment very much, as in the molecules *methyl acetate* CH_3COOCH_3 and *benzyl acetate* $CH_3COOCH_2C_6H_5$, where the moments are found to be 1·67 and 1·80 respectively.[62]

The moment of the *nitroso* group —N : O has been estimated as 3·14, and is larger in aromatic than in aliphatic compounds.[131,144,145] Sidgwick[132] has investigated the structure of the *azide* group $—N_3$. *Phenyl azide* $C_6H_5N_3$ has a moment 1·53, from which it appears that the azide group moment is about 1·5. Such a value was found to be compatible with ring structure for the group, but linear structure is indicated by the X-ray work on crystals, and ring structure is also excluded by arguments based on the heats of formation of organic azides.

It is finally concluded that a "resonance" mixture of $R-N=N\overset{\rightarrow}{=}N$ and $R-N\leftarrow N\equiv N$ must be present.

The influence of the solvent has been studied by Müller in the case of *chlorobenzene*. Since very few measurements are available on vapours, and nearly all the results depend on the solution method, a systematic study of this influence becomes important. It was found that considerable variation existed, the largest moment being found in hexane, and the least in carbon disulphide. Until the true nature of this influence is discovered, many difficulties must remain in interpreting the results of experiment. The uncertainty in assignment of dipole moments to organic molecules is often very considerable, and the development of the theoretical treatment is retarded (see this Vol.: 37D).

(ii) *Di-derivatives of Benzene.* Some averaged results on di-substituted derivatives of benzene are given in Table XLIX. Although the numbers are usually given to two decimal places, comparison between the results of different authors would indicate an uncertainty of at least ±0·1. The assigned separate group moments are in columns headed μ_X and μ_Y. These are mostly taken from measurements on mono-derivatives. Only cases where measurements are available on ortho-, meta- and para-derivatives are recorded in the table. The two leading groups are: (a) where the moment of the ortho-compound is the greatest, and that of the para-compound the least (17 cases); (b) where the moment of the para-compound is the greatest, and that of the ortho-compound the least (17 cases). There is also one case (c) where the meta-compound has the greatest moment ($C_6H_4(NH_2)_2$), and one case (d) in which that of the meta-compound is the least of the three ($C_6H_4(NO_2)(OCH_3)$). The molecules in groups (a) and (b) are arranged in descending order of moments of ortho-derivatives. The Roman No. references are to pages in the "Table of Dipole Moments."[43]

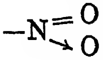
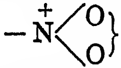
It becomes clear, on examination of Table XLIX, that for case (a) the moments contributed by the constituent groups have the same sign (μ_X and μ_Y either both positive or both negative); whilst, in case (b), the group contributions in the

TABLE XLIX.—DIPOLE MOMENTS OF DI-SUBSTITUTED DERIVATIVES OF BENZENE

Group	X	Y	ortho	meta	para	μ_x (= x)	μ_y (= y)	Reference
(a)	NO_2	CN	6 19	3 78	0 69	—3 94	—3 90	lxxii
	NO_2	NO_2	6 01	3 75	(0 32)	—3 94	—3 94	lxxii
	CHO	CHO	4 30	2 86	2 35	—2 8	—2 8	li
	NO_2	Br	4 09	3 29	2 45	—3 94	—1 52	lxxix
	NO_2	Cl	4 08	3 27	2 34	—3 94	—1 56	lxxviii, lxxix
	NO_2	CH_2Cl	4·00*	3 80*	3 56	—3 94	—1 82	134, lxxix, lxxx
	NO_2	I	3 79	3 33	2 84	—3 94	—1 27	lxxix
	Cl	CH_2Cl	2 31*	2 06	1 71	—1 56	—1 82	xxxii, xxviii
	Cl	Cl	2 35	1 44	(0 26)	—1 56	—1 56	xxxi
	Cl	Br	2 25	1 56	0·04	—1 56	—1 52	xxxii
	Br	Br	2 00	1·50	(0·25)	—1 52	—1·52	xxxi
	Br	I	1 80	1 14	0 49	—1 52	—1 27	xxxii
	CH_3	$OCOCH_3$	1 72	1 64	1 58	+0 45	—1 5	lii, 137
	Cl	C≡CH	1 68	1 38	0 96	—1 56	—0 56	135
	I	I	1 67	1·27	(0 27)	—1 27	—1 27	xxxi
	NH_2	CH_3	1 60	1·46	1 31	+1 55	+0 45	lxi
	CH_3	CH_3	0 54	0 39	0	+0 45	+0 45	xviii
(b)	NO_2	NH_2	4 35	4 83	6 1	—3 94	+1 55	lxxii
	CN	CH_3	3 79	4 19	4 37	—3 9	+0 45	lxi
	NO_2	CH_3	3 66	4 17	4 42	—3 94	+0 45	lxix, lxx
	NC	CH_3	3 35	3 96	4 75	—3 6	+0 45	136, lxi
	NO_2	OH	3 10	3 90	5 03	—3 94	+1 7	lxix
	NH_2	Cl	1 81	2 68	2 95	+1 55	—1 56	lxxvi
	NH_2	Br	1 77	2 65	2 93	+1 55	—1·52	lxxvi
	$COOCH_3$	CH_3	1·60	1 92	2 05	—1 9	+0 45	137
	Br	CH_3	1 44	1 75	1 94	—1 52	+0 45	xxv
	OH	CH_3	1 44	1·58	1 62	+1 7	+0 45	xlii, xliii
	Cl	CH_3	1 39	1·80	1 92	—1 56	+0 45	xxv
	Cl	OH	1 37	2 14	2 25	—1 56	+1 7	137, lxv
	OC_2H_5	OC_2H_5	1 37	1·70	1 75	+1 3	+1·3	lii, liii
	OCH_3	OCH_3	1 31	1 59	1 68	+1 2	+1 2	li
	I	CH_3	1 21	1·58	1·71	—1 27	+0·45	xxv
	OCH_3	CH_3	1 0	1·17	1 20	+1 2	+0·45	xliv
	$COOCH_3$	NH_2	1 0	2 4	3 3	—1 9	+1 55	lxx
(c)	NH_2	NH_2	1·45	1 80	1·52	+1 55	+1 55	lxii
(d)	NO_2	OCH_3	4 82	3 86	4 76	—3 94	—1 2	lxx, 138

* Free rotation hindered.

majority of cases have opposite signs. The results are then in general accordance with anticipation, for in the para-compounds where the group contributions are like in sign, the resultant moment will be given by their difference, and hence we may expect the para-compounds to have the smallest moment of the three (case (a)), whilst if the group contributions are of opposite sign, the effect will be additive in para-compounds, so that these may be expected to have the largest resultant (case (b)).

These considerations were originally applied in fixing the signs of the group moments. It only becomes necessary to fix the sign of one group ; others may be obtained from this by consideration of the appropriate para-compounds. We may commence with NO_2, which has been assigned the structure  $-\mathrm{N}\genfrac{}{}{0pt}{}{=\mathrm{O}}{\searrow\mathrm{O}}$: it then appears that the positive end of the dipole must be towards the N atom, since the O atom of the semi-polar double bond has received negative charge in acting as a Sidgwick "acceptor." The negative sign given to the NO_2 group moment (—3·94) then indicates that the negative end of the dipole points away from the benzene ring. In order that the group moments shall reinforce each other in para-nitraniline, it follows that the negative end of the NH_2 dipole must be nearest to the ring, so that this group moment is labelled positively (+1·55), and so on in other cases. It may be added that if para-dinitrobenzene has zero moment, the moment of the NO_2 group must act along the line bisecting the angle between the N–O valency directions, and that therefore the group must really be symmetrical, and cannot contain one semi-polar and one double bond as shown above. It may therefore be written  $-\overset{+}{\mathrm{N}}\left\langle\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}-$. This does not, of course, affect the argument by which the sign of the group was derived.

In general, it is found that for a normal covalency between two atoms, the negative pole lies towards the atom in the higher periodic group, as in the cases $H^+–Cl^-$, $C^+–Br^-$, $C^+–O^-$ and $N^+–O^-$. Sidgwick has suggested the designation H-+->Cl, where the crossed end of the arrow denotes the location of positive charge.

Attempts have been made to place the results upon a quantitative basis. Thomson[189] assumed the moment of the benzene ring to be zero, and that the angles between the directions of the group moments were 60°, 120° and 180° in ortho-, meta- and para-compounds respectively. If, then, the group contributions may be treated as vectors, the resultants can be calculated from the parallelogram of moments, using the relation $c^2 = a^2 + b^2 - 2ab\cos C$ derived in the trigonometrical solution of triangles (a, b, c sides, angle C opposite to side c) In the following, for convenience, μ_X and μ_Y are replaced by x and y respectively. The resultant moments are then as shown in the series of equations (11) :

$$\left.\begin{array}{l}\textit{Ortho-}\\ \textit{Meta-}\\ \textit{Para-}\end{array}\right\}\mu^2 = \left\{\begin{array}{ll} x^2 + y^2 - 2xy\cos(180 - 60) & = x^2 + y^2 + xy \\ x^2 + y^2 - 2xy\cos(180 - 120) & = x^2 + y^2 - xy \\ x^2 + y^2 - 2xy\cos 0 & = x^2 + y^2 - 2xy \end{array}\right\};$$

$$\mu = \left\{\begin{array}{l} \sqrt{x^2 + y^2 + xy} \\ \sqrt{x^2 + y^2 - xy} \\ x - y \end{array}\right\} \quad \ldots\ldots\ \ldots\ \ldots\ldots \quad (11)$$

It is further observed that for equal substituent groups ($x = y$), the μ's reduce to $\sqrt{3}x$, x and 0 for the three cases respectively. Account must be taken of sign in making the substitutions. Thus Kerr[140] pointed out that, in the case of the *chlorotoluenes*, if x for CH_3 is taken positively, y for Cl must be taken negatively. Allowance for sign is made in Table XLIX.

Comparison between calculation and experiment for three examples of each of cases (a) and (b) is made in the following scheme :

	Cl–Cl		NH_2–CH_3		CH_3–CH_3		Cl–CH_3		NO_2–CH_3		NO_2–NH_2	
Ortho-	2·70	2·35	1·63	1·60	0·78	0·54	1·39	1·39	3·74	3·66	3·44	4·35
Meta-	1·56	1·11	1·19	1·46	0·15	0·39	1·83	1·80	4·18	4·17	4·90	4·83
Para-	0	(0·26)	0·90	1·31	0	0	2·01	1·92	4·39	4·12	5·49	6·1
	calc	obs	calc	obs	calc.	obs	calc	obs	calc	obs.	calc	obs
	case (a)						case (b)					

It is observed that calculation places the moments in the right order in the two cases (a) and (b) examined. On the other hand, the agreement is not always as good as might be expected, but it may be remembered that the measured values are subject to considerable errors of the order ±0·1 unit.

Deviations which cannot be attributed to experimental uncertainty have been accounted for as due to either (i) interaction between substituent groups, in which is included inductive effects upon each other and upon the benzene ring, or (ii) deviations from the angles 60°, 120° and 180° between the vector moments. Cause (i) has been specially applied to ortho-compounds, and (ii) to para-compounds, though in general the two cannot be sharply separated.

When both substituent groups make contributions of the same sign, repulsion between them may cause the angles in the ortho- and meta- positions to be greater than 60° and 120° respectively, and smaller moments may be observed than are given by calculation (compare the *dichlorotoluenes* in the above scheme). Conversely, when the signs are opposite, attraction may lower the experimental moments as compared with calculation. This appears in the case of *orthonitroaniline* (last column of above scheme). Even in the para-position, attractions between the groups may cause the observed moments to exceed those found theoretically.[141]

Stuart[142] found that the varying heats of combustion of isomeric benzene derivatives yielded evidence of "internal molecular potential," associated with attractions and repulsions between substituent groups, partly resulting from interaction of dipoles and partly from polarization of the benzene ring by the substituents. Smallwood and Herzfeld[143] attempted to take account of inductive effects. The results were concordant only where the dipoles may be assumed to be situated at the circumferences of the C atoms of the benzene ring, that is, at the conventional valency bonds.

The large contribution to molecular moments made by nitro-groups has been associated with "semi-polar" structure, represented by $O = N^+–O^-$, where the nitrogen atom has given up an electron to one oxygen atom. Similarly, the nitroso-group $—N^+—O^-$ makes a large contribution. The moment of *nitrosobenzene* has been estimated as 3·22[144] and 3·14.[145] *Paranitrosomethylaniline*, $NHCH_3C_6H_4NO$, has a moment of 7·38, apparently the largest value so far recorded for any organic compound.[145] *Paranitrosophenol*, OHC_6H_4NO, has a higher moment (4·72) than the additive moments of the ring substituents, from which it appears that the nitroso-group has the capacity of promoting the polarization of the molecule as a whole.[131]

Bergmann, Engel and Sändor[146,147] have tested the applicability of the equations (11) in a large number of cases. Generally satisfactory results are obtained when the groups are taken from the list Cl, Br, I, CH_3, NO_2, except for ortho-compounds, where distortion is assumed, and the angle θ calculated from the formula

$$\mu = \sqrt{x^2 + y^2 - 2xy\cos(180 - \theta)} \quad \ldots\ldots\ldots \quad (12)$$

μ being the observed moment. The following values were obtained · NO_2–CH_3 60°, Cl–CH_3 60°; NO_2–NO_2 79°; Cl–Cl 86°; Cl-NO_2 97°; Br–Br 101°; CH–CH_3 103°; I–I 104°; Br–I 106°. The effect of repulsion between like groups in ortho-compounds is clearly observed. In other cases, where the groups OH, OR, CHO, COR, COOH, COOR are present, deviations from the demands of equation (11) may be expected on the ground that the groups are " bent," so that the valency direction to the ring carbon does not coincide with the direction of the resultant group moment. Wolf[148] assumed the angle 110° for the OCH_3 group. Where these groups are present, zero moment will not be expected for the symmetrical para-compounds RC_6H_4R, as is found in the following cases: R = OCH_3 1·8; OC_2H_5 1·7; CHO 2·35; $COOCH_3$ 2·2; $COOC_2H_5$ 2·3. Bergmann termed such groups as " irregular," as distinct from those in which the moment vector lies along the valency direction to the ring carbon atom. Compounds of the type XC_6H_4Y, where X is irregular and Y regular, were considered. If the angle between the moment of X and the valency direction is ϵ, we have

$$\mu = \sqrt{x^2 + y^2 - 2xy\cos\epsilon} \quad \ldots\ldots\ldots\ldots\ldots \quad (13)$$

Using the case of *parachlorophenol*, ($\mu = 2{\cdot}4$, $x = 1{\cdot}7$, $y = 1{\cdot}5$), the angle ϵ for the OH group was found to be 83° 25′. From other corresponding compounds, the following angles were derived: OCH_3 67° 25′; CHO 141°; COOH 114° 50′;

$COOCH_3$ 180°. Other angles determined by this method are: NH_2 40°[149,150,151]; NCS 0°[149]; OH 90°[138,151]; OCH_3 90°[138]; 80°±10[151]; CH_2Cl 119°[152]; $COCH_3$ 50°[153]. Wolf[154] finds that angle estimations by Bergmann's method may be liable to errors as great as 10%. Bennett and Glasstone[155] hold that an additional moment operates along the axis of the benzene nucleus, rendering the method of calculation of valency angles inaccurate. The suggestion that departure from linearity of compounds of the phenol and anisole types might account for deviations between calculation and experiment was made by Williams[156] and Hojendahl.[50]

According to Sidgwick and collaborators,[157] the CN and NC groups have oppositely directed moments. Poltz,[136] on the other hand, holds that the moments are in the same direction. Reference to Table XLIX seems to support the latter view, since the moments of CN–CH_3 and NC–CH_3 di-derivatives both increase in the sense ortho—meta—para ((Group (b)).

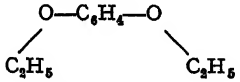
Fuchs[158] has proposed the general formula

$$\mu = \sqrt{x^2 + y^2 + 2xy\cos\alpha\cos\beta\cos\gamma} \quad \ldots\ldots \quad (14)$$

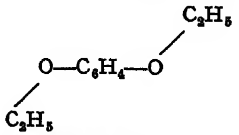
where α, β are the angles of inclination of the substituent group moments to the valency directions, and γ is the angle between the valency directions (60° for ortho-, 120° for meta-, and 180° for para-compounds). The equation reduces to the standard forms of equation (11) for the case $\alpha = \beta = 0$. Donle[137] has applied the formula to the isomerides of *methyl toluate*, $CH_3C_6H_4COOCH_3$, and *benzoylcresylether*, $CH_3C_6H_4OCOCH_3$, with satisfactory results (moments in Table XLIX).

It appears that three leading causes of difference between calculation and experiment for the moments of benzene di-derivatives may arise. Each of them involve distortion from the requirements of the perfect symmetry of the unsubstituted benzene ring: (i) repulsion between like directed moments, and attraction between oppositely-directed moments; (ii) "natural" valency inclinations, as of the oxygen and nitrogen atoms; (iii) "space-filling" requirements, whereby large groups may cause displacement of their neighbours, especially in ortho-compounds. Lütgert[159] has attributed deviations between theory and experiment in the *ortho-halogennitro*-di-derivatives to (iii). It is clear that all these interfering influences are likely to be most operative in ortho-compounds, where the substituents approach each other most closely.

The rotation of groups, whether hindered by interaction or otherwise, has also been taken into account in connection with the moments of di-derivatives of benzene. Thus Eucken and Meyer[118] early calculated the moments of the *cis*- and *trans*-positions of *hydroquinone diethylether*, which may be depicted as follows:



(*cis*-position)



(*trans*-position)

The moments were found to be 1·9 and 0 for the *cis*- and *trans*-positions respectively, assuming the oxygen valency angle to be 110°, which more recent work has indicated to be too large. The observed moment is about 1·7. Werner[181] thought he had evidence of a temperature variation of moment for this compound, which would indicate hindrance of free rotation due to interaction between the two ethoxy-groups, as in the case of ethylene dichloride previously discussed. Subsequent work by Hassel and Næshagen[182] and Kamerling and Smyth[160] has not confirmed this observation. Further, Weissberger and Sängewald,[161] assuming free rotation of the groups, showed that the moment of *hydroquinone dimethylether* could be calculated from the moment of anisole, assuming an oxygen valency angle of 90°. The formula for the resultant of two moments inclined at an angle of 90° will be $\sqrt{2}x$. Inserting the moments of anisole and phenetole as 1·16 and 1·28 respectively, we obtain the resultants 1·64 (expt. = 1·73) and 1·80 (expt. = 1·72) for the dimethyl and diethyl ethers of hydroquinone. The group rotations are therefore unhindered. In other cases, hindered rotation is found for ortho- (and sometimes meta-) compounds. Fairbrother[162] has found that the moments of ortho- and meta-*nitrobenzylchlorides*, $NO_2C_6H_4CH_2Cl$, increase somewhat with temperature between 20° and 120°, indicating hindrance of free rotation. No variation with temperature was detected for the para-compound. Similar results have been recorded in the case of the *chlorobenzylchlorides*.[163]

The moment of *mononitrohydroquinone diethylether* can be calculated on the assumption that the nitro-group is in the plane of the ring to which it is attached, the acetyl group moments being at right angles to the plane. Taking the moment of the unsubstituted diethylether as 1·7, the resultant will be $\mu = \sqrt{3{\cdot}9^2 + 1{\cdot}7^2} = 4{\cdot}3$ (compare the experimental value 4·56).[174]

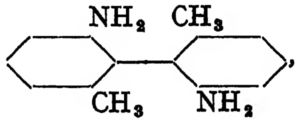
(iii) *Higher Derivatives of Benzene.* The moments of symmetrical tri-derivatives of benzene have been given as follows: *trichlorobenzene* 1.3.5. $C_6H_3Cl_3$ 0·28;[164] *tribromobenzene* 1.3.5. $C_6H_3Br_3$ 0·28;[164] *mesitylene* 1.3.5. $C_6H_3(CH_3)_3$ 0·07; *trinitrobenzene* 0·70.[164] It is possible that these small though definite moments may be accounted for by the attached groups not lying exactly in the plane of the benzene ring. According to Parts,[165] the moment of the tri-nitro-compound is only of the order 0·8 if atom polarization P_A is absent. A more recent determination has yielded the smaller moment 0·41[166] The less symmetrical 1.2.4. *trichlorobenzene* has the higher moment 1·25.[167] Lutgert[168] has calculated the angles between the substituent groups for compounds of this type.

Amongst the tetra-substituted compounds, 1.2.3.5. *tetrachlorobenzene* has a moment estimated to be less than 0·65.[167] Brown and co-workers[169] have examined derivatives of mesitylene of the type $C_6H_2(CH_3)_3X$, with the following results: X = F 1·36; Cl 1·55, Br 1·52; I 1·42, OH (mesitol), 1·36. The measurements were made in benzene solution at 30°C. It is noteworthy that the moments increase in the sense F→Cl→Br→I, and apparently only the mono-derivatives of methane and benzene have a lower moment for the F than for the Cl compounds. Taking the moment of fluorobenzene as 1·46, the moments calculated for the substituted mesitylenes agree with calculation by the method of Smallwood and Herzfeld.[143] An exception was found in the case of the nitro-compound (X = NO_2), where the assigned moment is 3·64.

According to Tiganik,[164] the moments of *hexamethylbenzene* and *hexachlorobenzene* are small though definite, equal to 0·1 and 0·2 respectively. Further, tri-derivatives of mesitylene were found to have moments; for $C_6(CH_3)_3X_3$, when X = Cl 0·38; Br 0·35; NO_2 0·79. It was found that these moments were additive: thus the sum of the values of $C_6H_3(CH_3)_3$ and $C_6H_3X_3$ gave the moment of $C_6(CH_3)_3X_3$: for X = Cl, 0·28 + 0·07 = 0·35; Br 0·28 + 0·07 = 0·35; NO_2 0·70 + 0·07 = 0·79, agreeing closely with the experimental values shown above. Lütgert,[170] however, finds that the moments of tribromo- and trinitro-mesitylene are zero, in opposition to the result of Tiganik. The moment of *tribromotrinitromesitylene* is also found to be zero, and it is suggested that such cases may be explained by the groups of different kinds being bent on opposite sides of the benzene ring, whilst tribromo- and trinitromesitylene have plane ring structures. It has not infrequently happened that small reported moments for apparently symmetrical compounds have been subsequently found to be zero. In cases where a small moment is definitely found in benzene solution, the possibility of compound formation with the solvent must not be overlooked: thus an unsymmetrical formula has been assigned to a supposed compound between benzene and trinitrobenzene.[171]

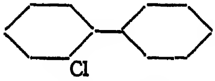
(d) *Diphenyl and related Compounds.* The case of *diphenyl* ($C_6H_5C_6H_5$) and its 4.4′ derivatives was discussed by Adkins, Steinbring and Pickering,[172] Kuhn and Albrecht,[173] and Williams.[156] Diphenyl has vanishingly small moment, in which respect it is unlike some of its symmetrically substituted di-derivatives (see below). It may be noted here that the model for diphenyl suggested by Kaufler,[175] where the rings lie over each other in parallel planes, has not received any adequate support in more recent work (see, however, this Vol.: 14Ab). The argument for a folded structure of *benzidine* (4 4′ $NH_2C_6H_4C_6H_4NH_2$) rested upon a small, perhaps zero, moment for paraphenylene diamine ($C_6H_4(NH_2)_2$), since benzidine has definite moment (about 1.3). Later work showed that paraphenylene diamine had finite moment (μ = 1·52), so that this argument in favour of folded rings in diphenyl became invalidated [176]

Induction in the benzene rings on substitution in diphenyl is indicated by comparison with corresponding mono-derivatives of benzene. Thus amongst the *nitrodiphenyls,* the ortho- and meta-compounds have lower, and the para-compound higher, moment than nitrobenzene.[177] The ortho-compounds give the least good agreement between experiment and the vectorial addition of group moments. Further evidence of polarization of benzene nuclei has been obtained by the study of the moments of *mono-* and *di-chlorodiphenyls.*[180]

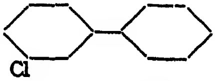
According to Bergmann and Engel,[178] in 6.6′ *diamino-2.2′ ditolyl* 

, substitution in the two ortho-positions in each benzene ring causes hindrance of free rotation, the rings being turned about the central connecting link through an angle of 67°. The compound exhibits optical activity. In 4.4′ *dicyanodiphenyl* ($CNC_6H_4C_6H_4CN$), where a moment of 1·14 has been recorded, it may be supposed that CN is an "irregular" group, the direction of the C–N linkages being inclined at an angle to the direction of the C(of CN)-ring linkages.[179]

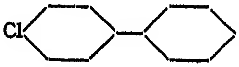
The moments of *mono-chlorodiphenyls* have been determined as follows :—[180]



I. $\mu = 1{\cdot}30$



II $\mu = 1{\cdot}79$

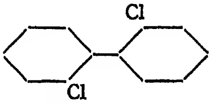


III. $\mu = 1{\cdot}53$

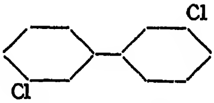
The para-substituted compound (III) has about the same moment as chlorobenzene, suggesting that the diphenyl link makes zero contribution, as in diphenyl itself. However, when the C–Cl group moment is taken as 1·55, it is impossible to reproduce the experimental values for compounds I and II unless the central link has a moment with the negative end towards the substituted ring. It is possible, of course, that the

C–Cl link makes different contributions according to its position.

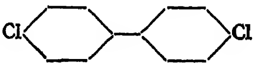
Difficulties also arise with the *di-chlorodiphenyls* shown below :—[180]



IV $\mu = 1{\cdot}77$



V. $\mu = 1{\cdot}68$



VI. $\mu = 0$

The compound VI has zero moment, in accordance with anticipation, but calculation for compounds IV and V indicate that they should have the same moment, equal to 1·92 ; actually, neither of them attains this value, and the moment of IV is greater than that of V. It appears that the variations must be attributed to polarization effects, which are as yet imperfectly understood.

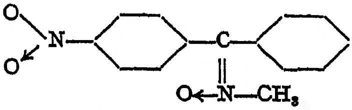
Cases where atoms or groups intervene between the two rings in diphenyl are next considered. The moment of *diphenyl ether* $(C_6H_5)_2O$ has been found to be 1·05,[183] and of *diphenyl sulphide* $(C_6H_5)_2S$ 1·47,[184] and these are associated with the natural inclination of the O and S valency directions. The O angle θ in diphenyl ether has been calculated as follows :—[183]

$$\begin{array}{lllr} \text{From} & (C_6H_5Br), & \mu(\text{C–H}) + \mu(\text{C–Br}) = 1{\cdot}50 & \text{(a)} \\ & (C_6H_5)_2O, & 2[\mu(\text{C–H}) + \mu(\text{C–O})]\cos\theta/2 = 1{\cdot}05 & \text{(b)} \\ & (p\text{–}BrC_6H_4)_2O, & 2[\mu(\text{C–Br}) - \mu(\text{C–O})]\cos\theta/2 = 0{\cdot}6 & \text{(c)} \end{array}$$

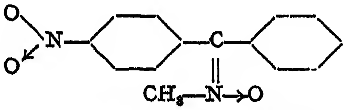
whence, adding (b) and (c) and substituting (a), $3{\cdot}00\cos\theta/2 = 1{\cdot}65$, giving $\theta = 113°$, is obtained. A similar calculation gave $\theta = 142°$ for diphenyl sulphide. Hampson, Farmer and Sutton[185] have calculated the angles between the oxygen valency directions, using the method of Hampson and Sutton,[126] in the following cases : diphenylmethane 115°, diphenyl ether 142°, anisole 150°, phenol 137°, dimethyl ether 147°, and water 134°. The S angle in diphenylsulphide is found to be

118°. The estimates for ethers are generally higher, and for sulphides lower than those previously found.

Hydrazobenzene, $C_6H_5NHNHC_6H_5$, is assigned the moment 1.53.[186] This points to a *cis*-configuration, in opposition to views expressed by Bergmann and co-workers.[187] *Benzophenone*, $C_6H_5COC_6H_5$, has a large moment, given as 3.13[188] and 2.95.[189] In the substituted *diphenylacetylenes* $(C_6H_5)_2C : CX_2$, the angle between the X groups increases with greater space requirements of the substituents : X = NO_2 96°, Cl 110°, Br 114°, whilst the moments correspondingly decrease : 5·49, 1·79, 1·62.[189] Deviations from tetrahedral symmetry of the C valencies are a measure in such cases of the space requirements of the substituent groups. *Dianisylmethane* $(CH_3OC_6H_4)_2CH_2$, *dianisylketone* $(CH_3OC_6H_4)_2CO$ and *dianisylthioketone* $(CH_3OC_6H_4)_2CS$ have the moments 1·61, 3·90 and 4·44 respectively. In general, aromatic ketones and thioketones have higher moments than corresponding aliphatic compounds.[190] The moments of stereoisomeric *stilbene dichlorides*, $C_6H_5CHClCHClC_6H_5$, indicate that free rotation is hindered about the central C–C linkage, as in the case of ethylene dichloride previously discussed.[191] The meso- form of *hydrobenzoin*, $C_6H_5CHOHCHOHC_6H_5$, has the moment 2·06, whilst the racemic mixture form has the higher moment 2·67.[192] On the other hand, the dextro and racemic forms of *dimethyl tartrate* have essentially the same moments (2·93 and 2·92 respectively).[192] Observations on certain aromatic compounds of the oxime type are in agreement with the theory of their geometrical isomerism. The *syn-* and *anti-N.-methylethers* of *paranitrobenzophenone oxime* have the moments shown below their formulæ :—



syn–form $\mu=6{\cdot}60$



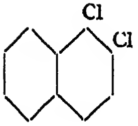
anti–form $\mu=1{\cdot}09$

It is observed that where the N → O links, which tend to confer moment to the molecule, are on the same side the moment is much greater than where their effects partly compensate each other.[193] Parsons and Porter[194] have studied six *oximes* of *monochlorobenzophenone* (three pairs of *cis*- and *trans*-isomers). The two ortho-compounds have equal moments: the higher melting meta- and para- compounds have lower moments. It is sometimes possible to assign configurations (*syn*- or *anti*-) to oximes on the basis of dipole moment measurements.[195] The early work on the *cis*- and *trans*-dichloroethylenes may be recalled in this connection (this Vol.: 38C).

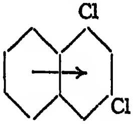
(e) *Naphthalene and its Derivatives.* The dipole moment of *naphthalene*, $C_{10}H_8$, containing two "condensed" benzene rings has been shown by Parts[196] to be zero. This has been confirmed by Puchalik,[197] who found that the Maxwell relation $\epsilon = r^2$ was obeyed. The naphthalene molecule may therefore be considered to be symmetrical and planar.

Parts[196] investigated *mono-halogen substituted* derivatives of naphthalene, and found that the α-derivatives had lower moments than the β-derivatives. The same was shown to be true for α- and β-naphthols.[197] The general conclusion has been drawn that different group moments must be assigned to the two positions, the group moment in α-compounds being that expected for aromatic substitution, whilst that in β-compounds corresponds more closely to aliphatic substitution. It may be added that Br and Cl substitution gives rise to the same moments, the same being true of F and I: α–F and α–I, 1·42; β–F, β–I, 1·56; α–Cl, α–Br, 1·59; β–Cl, β–Br, 1·72.

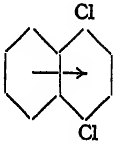
The *di-chloronaphthalenes* have been studied experimentally and theoretically by Weissberger and co-workers.[180] It is pointed out that in the case of the naphthalene nucleus, unlike that of diphenyl, an advantage arises, in that the benzene residues are held together and cannot rotate relatively to each other. Measurements were made on seven of the ten possible isomers, with results as given below. The numbers in brackets are calculated, on the assumptions that α–Cl and β–Cl have the respective group moments found by Parts of 1·59 and 1·72, and that the valency directions are inclined at 60°, 120° or 180°.



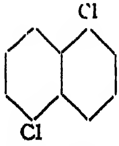
I. μ = 2·44 (2·87)



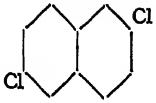
II. 1 85 (1·66)



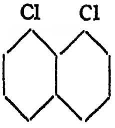
III 0·50 (0)



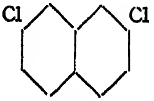
IV. 0·0 (0)



V. 0·2 (0)



VI 2·88 (3·18)



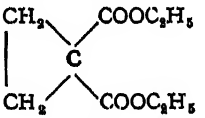
VII. 1·52 (1·72)

In compounds I and VI, the calculated values are greater than those observed. This may be associated with the "ortho-effect" previously noted in connection with benzene di-derivatives. The calculated values for II and III, however, lie below the observed values, an effect which is only noticed where both substituents are in the same ring. It may be accounted for by a shift of electrons towards the substituted ring, equivalent to a small component of polarization moment in the direction shown by the arrows in the above figures. Assuming that this polarization moment is of the order 0·2, the calculated values become (II) 1·83, (III) 0·40, giving good agreement with experiment. This point of view finds support in the observation that when the substituents are symmetrically placed in different rings, as in IV and V, the group moment is vanishingly small, the polarizing effects of the two Cl's just neutralizing each other. In compound VII, which has no centre of symmetry, we shall expect resultant moment, in agreement with experiment. The calculated value is too large, but agreement may be obtained by combining two aromatic group moments inclined at 120°. It does not appear clear, however, why the aliphatic group moment used for the β-positions will not bring about coincidence with experiment, but at least the absence of polarization between the rings when the substituents are in different benzene residues seems confirmed. An attempt is made by the authors to extend these considerations to anomalies in the group of dichlorodiphenyls noticed above.

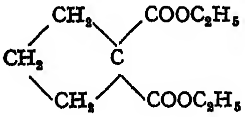
On account of inductive influences by the NO_2 group in the naphthalene nucleus, measurements of dipole moments in molten naphthalene may yield smaller values for nitro-compounds than when the same compounds are dissolved in benzene.[198] It appears that molecular compounds are formed, for example, between dinitrobenzene and naphthalene. Induction effects are thus generally larger in naphthalene, other things being equal, than in benzene.

(f) *Organo-metallic Compounds.* A list of determinations on these compounds is given at the end of the "Table of Dipole Moments."[43] Early work was done by Bergmann and Schütz.[199] *Mercury diphenyl,* $C_{12}H_{10}Hg$, has been shown by Hampson[200] to have a small, but probably real, moment of about 0·5 in decalin solution It is suggested that the Hg–C link is flexible, having an angle of swing about a mean position. Consideration of para-substituted derivatives, in which the moments are greater than that of mercury diphenyl itself, suggests that the Hg–C link constitutes a small dipole, with the negative pole towards the Hg atom. This is contrary to the general rule that with a normal covalency between two atoms the negative pole is towards the atom in the higher periodic group (see 39Ac(ii) above), but Hampson holds that since this rule is derived for atoms with completed quantum groups, it would not be surprising if it did not apply for di-covalent Hg with only 4 electrons in its outer quantum shared group.

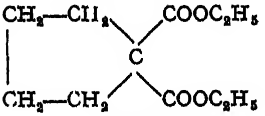
(g) *Other Ring Systems.* The dipole moments of *cyclic* 1 : 1 *dicarboxylic esters* have been determined by Farmer and Wallis[201] as follows :—



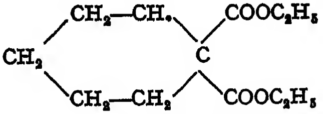
$\mu = 2{\cdot}40$



$\mu = 2{\cdot}22$



$\mu = 2{\cdot}14$

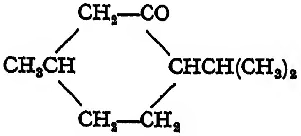


$\mu = 2{\cdot}23$

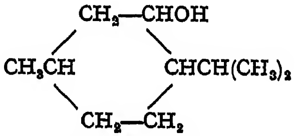
The compound with the five-membered ring has the lowest dipole moment in the series. The authors hold that the results are not in accordance with the external valency angles for rings of different sizes put forward by Beesley, Ingold and Thorpe, the moments for 3-, 4- and 5-membered rings changing in the sense opposite to that predicted by the theory.

Cyclohexane has zero moment, as anticipated from the symmetrical ring structure $(CH_2)_6$.[43] With *cyclohexanol* $(CH_2)_5CHOH$, the asymmetry caused by OH substitution, gives a moment of 1.69.[202] Other derivatives of cyclohexane have been examined.[43]

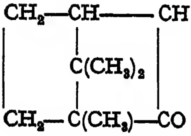
The moments of a number of ring compounds containing the CO and CHOH groups, *menthone* (I),[190,204] *menthol* (II),[203] *camphor* (III),[190,204] *borneol* (IV),[203] *fenchone* (V),[190,204] *fluorenone* (VI)[189] and *2-nitrofluorenone* (VII)[189] have been examined. It appears that the moment of CO in a five-membered ring differs somewhat from that in other ketones.[204]


CH_2—CO
CH_3CH
$CHCH(CH_3)_2$
CH_2—CH_2

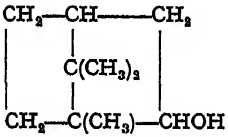
I. $\mu = 2\cdot82$


CH_2—CHOH
CH_3CH
$CHCH(CH_3)_2$
CH_2—CH_2

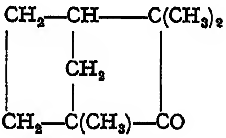
II $\mu = 1\cdot54$


CH_2—CH——CH_2
$C(CH_3)_2$
CH_2—$C(CH_3)$—CO

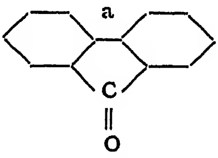
III $\mu = 2\cdot94$


CH_2—CH——CH_2
$C(CH_3)_2$
CH_2—$C(CH_3)$—CHOH

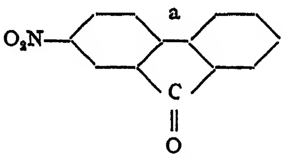
IV. $\mu=1\cdot56$


CH_2—CH——$C(CH_3)_2$
CH_2
CH_2—$C(CH_3)$—CO

V. $\mu = 2\cdot91$



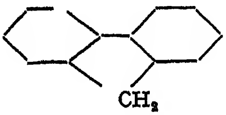
VI. $\mu = 3\cdot29$



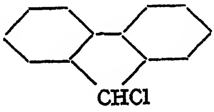
VII. $\mu = 5\cdot44$

The reduction of moment in replacing CO by CHOH is seen in the change from I to II, and from III to IV. The isomers III and V do not differ very greatly in moment. The alcohols II and IV have similar moments, which are of the same order as those of aliphatic alcohols, so it appears that the ring system has no measurable influence on moment.[203] In VI and VII, it is found that of the five-carbon ring valencies that of the diphenyl linkage (marked a) is the weakest.[189] Induction effects do not apparently play a large part in these ring systems.

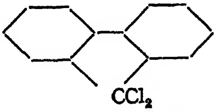
Fluorene (VIII), and its substituted compounds, 9-*chlorofluorene* (IX), 9-*dichlorofluorene* (X) and 2.7-*dibromofluorene* (XI) have been examined by Bergmann, Engel and Hoffmann,[205] with the following results :—



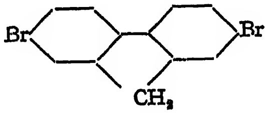
VIII. $\mu = 0$



IX. $\mu = 1{\cdot}76$



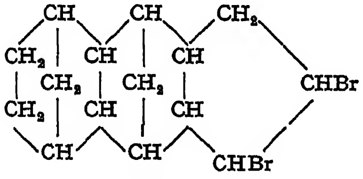
X. $\mu = 1{\cdot}85$



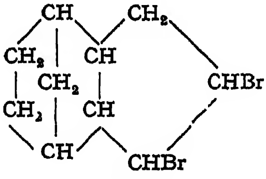
XI. $\mu = 0$

The zero moment of fluorene (VIII) suggests a planar structure. This seems confirmed by the zero moment of XI, where the two C–Br valencies must be in a straight line so as to neutralize each other. The moment of IX is half-way between the value for aromatic (1·56) and aliphatic (1·96) C–Cl linkages, suggesting a C–Cl linkage intermediate in character between the two types. If, now, in X we assume tetrahedral symmetry for the directions of the two C–Cl valencies, it is possible to calculate what group moment for C–Cl will yield the resultant 1·85; this comes out to be 1·60, which is nearly equal to the value for an aromatic C–Cl (1·56). Hence the linkages in X are nearer to the aromatic than the aliphatic types, and this is found to be borne out by the chemical and physical relations of the compound. Reverting to 2-nitrofluorenone (VII), the evidence from XI suggests that the NO_2 and CO moments will be perpendicular to each other, unless some deformation occurs. Taking the moments of VI and VII, and that of the NO_2 group (3·98), the angle between the valencies is 86°, suggesting a very slight compression exerted by the substituent NO_2 so that the diphenyl rings are not strictly in linear axial relation in VII.

Donle[206] has studied derivatives of di- and tri-cyclopentadiene prepared in 1932 by Alder and Stein. The molecules have a puckered structure, which leads to the existence of α- and β-stereoisomerides. The tri-cyclopentadienes contain two double bonds, which may be saturated by hydrogen and bromine respectively. The resulting compounds exist in *cis*- and *trans*-forms due to alteration in the relative positions of the Br atoms. Three *dihydrotricyclopentadiene dibromides* (*α-cis*, *β-cis*, *β-trans*) are represented by XII, whilst XIII depicts *dihydrodicyclopentadiene* cis-*dibromide*. The observed and calculated moments are shown below the structures.



XII.



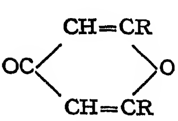
XIII

	α-cis	*β-cis*	*β-trans*	*cis*
μ (obs.)	3·20	3·18	1·92	3·14
μ (calc)	3·76	3 76	1·85	3 76

The calculated values are too high for the *cis*-, and about right for the *trans*-compounds. The moments of the three *cis*-compounds are about equal, from 3·14 to 3·20, and greater than the moment of the *trans*-compound (1·92), in accordance with expectation for geometrical isomerism. The complex ring systems appear to exert little influence on the resultant moment.

(B) **Heterocyclic Division.** (a) *Compounds containing Oxygen or Sulphur. Dimethyl γ-pyrone* (R = CH_3 in I), *dimethylthio γ-pyrone* (R = CH_3 in II) and *diphenyl γ-pyrone*

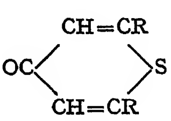
($R = C_6H_5$ in I) have been examined by Hunter and Partington.[207] *Thianthrene* (IV) was investigated by Walls and Smyth[208] and by Bennett and Glasstone.[209] Results are given below.



I.

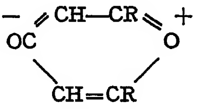
$R = CH_3$
μ = 4·05

$R = C_6H_5$
μ = 3·82

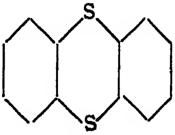


II.

$R = CH_3$
μ = 5·05



III

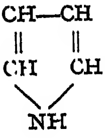


IV.

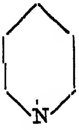
μ = 1·50 (1·41)

On account of the circumstance that the moments of the γ-pyrones cannot be reproduced from the additive group moments of –O– and =CO, a polar formula of Type III has been proposed.[207] The moment of IV indicated that the two benzene rings are not in one plane, but are inclined about the line joining the two S atoms.[209] The moment given by Bennett and Glasstone is adopted, the measurements being made in CS_2 and CCl_4 solution.

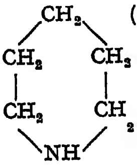
(b) *Compounds containing Nitrogen.* The following cases are selected for consideration: *Pyrrole* (I),[210] *pyridine* (II),[211] *piperidine* (III),[211] *α-picoline* (IV),[211] *β-picoline* (V),[211] *collidine* (VI),[211] *quinoline* (VII),[211] *isoquinoline* (VIII),[211] *quinaldine* (IX),[211] *pyrazine* (X),[212] 2.5 *dimethylpyrazine* (XI),[212] 2.6-*dimethylpyrazine* (XII),[212] 2.3-*dimethylquinoxaline* (XIII),[212] and *α-methylquinazoline* (XIV).[212] Results are as given below the formulæ.



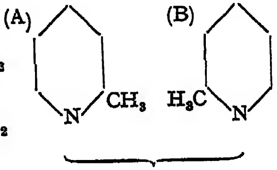
I. μ = 1·83



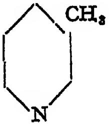
II. μ = 2·26



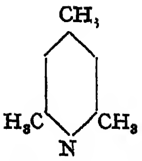
III. μ = 1·17



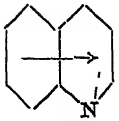
IV μ = 1·72



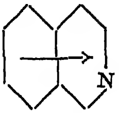
V. μ 2·30=



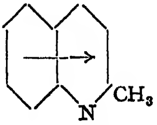
VI. $\mu = 1\cdot93$



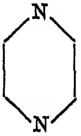
VII. $\mu = 2\cdot16$



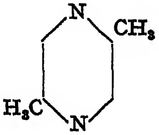
VIII. $\mu = 2\ 54$



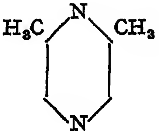
IX $\mu = 1\cdot86$



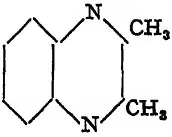
X $\mu = 0$



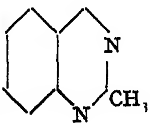
XI. $\mu = 0$



XII. $\mu = 0\cdot53$



XIII. $\mu = 0$



XIV. $\mu = 2\cdot2$

The moment of II (pyridine) can be very accurately reproduced by assuming the group moments C–H = 0, C–N = 1·3, C=N 2·6. The moment μ is given by

$$\sqrt{1\cdot3^2 + 2\cdot6^2 + (2 \times 1\cdot3 \times 2\cdot6\cos120^\circ)} = 2\cdot25$$

(expt. = 2·26), and acts along the dotted line shown, being directed towards the N atom by the convention already explained (the N = C bond is supposed to lie to the right of the N atom). When a similar calculation is applied to IV, it becomes evident that two cases (A) and (B) must be considered, which may be supposed to be present in a state of dynamic equilibrium. Assuming the group moment for CH_3 as 0·4, (A) gives 2·29, and (B) 1·92 by vector addition. Neither of these numbers agrees with experiment (1·72), but when they are composed vectorially, the resultant is 1·78, in close approximation with observation. Similarly, V has two forms (not shown), whose moments may be found to be 2·61 and 2·29, yielding the resultant 2·18 (compare expt. 2·30). The moment of γ-picolin, with the methyl group in para-relation to the N atom, can be predicted as 2·35 by a similar calculation, but here no experimental check is available. In VI, five vectors must be compounded together: the resultant is 1·95 (expt. 1·93). For compounds VII, VIII and IX, it is found that calculation and experiment do not agree unless a small polarization moment in the direction of the arrow is assumed to exist.

This result is analogous to that found in the dichloronaphthalenes (39Ae above). If in VIII, a moment of 2·25 acts along the dotted line towards the N atom, as in II, then the polarization moment must be 2·54 − 2·25 = 0·29. When this moment is applied to VII and IX, composition of the vectors gives 2·12 for VII (expt. 2·16), and 1·86 for IX (expt. 1·86). The results are thus in very satisfactory agreement with observation.[211] No detailed discussion appears to have been given to the pyrazines (X to XIV), but doubtless similar treatment would be effective. The zero moments of X, XI and XIII are understandable on symmetry grounds. A small moment appears for XII, which is asymmetric with respect to the centre of symmetry, whilst a large moment is observed for XIV, which is evidently the most unsymmetrical member of the group.

40. Dipoles and Association

(A) **Pure Substances.** Estimates of $P_A + P_O$ values for the vapours of HOH, CH_3OH and C_2H_5OH are about equal, suggesting that water behaves as a member of the alcohol series in the gas state.[213] Assuming that P_A does not vary very much in the series, P_O may be presumed to remain constant; so that dipole moment is not greatly affected by length of chain. The polarization drops when a gas becomes liquid, the decrease being greater for smaller molecules, when a series of similar compounds is compared. Thus, in the above case, the values of ΔP at the boiling points are 42·5, 26·0 and 15·1 for *water, methyl* and *ethyl alcohols* respectively. The fall in polarization on liquefaction has been associated with the linking together of dipoles in the liquid state. Figure LXXXIV shows how this may occur. In cases (a) and (b), the dipoles set themselves in such ways as to tend to neutralize each other's influence, with a consequent lowering of polarization; in case (c), the dipoles reinforce each other, with increased polarization. The association of water and the alcohols in the liquid state may then be represented by (a). Now suppose a liquid to be completely associated according to type (c), with *n* molecules in each aggregate. Then the total number of molecules, originally N, becomes N/n, and the pole strengths become $n\mu$ instead of μ The expression for b in equation (4) is therefore increased n times, for the variable part $N\mu^2$ becomes $N(n\mu)^2/n$, or $nN\mu^2$.

The factors determining the degree of dipole association appear to be: (1) the sizes of the molecules; (2) the geometrical lie of molecules in juxtaposition.[213]

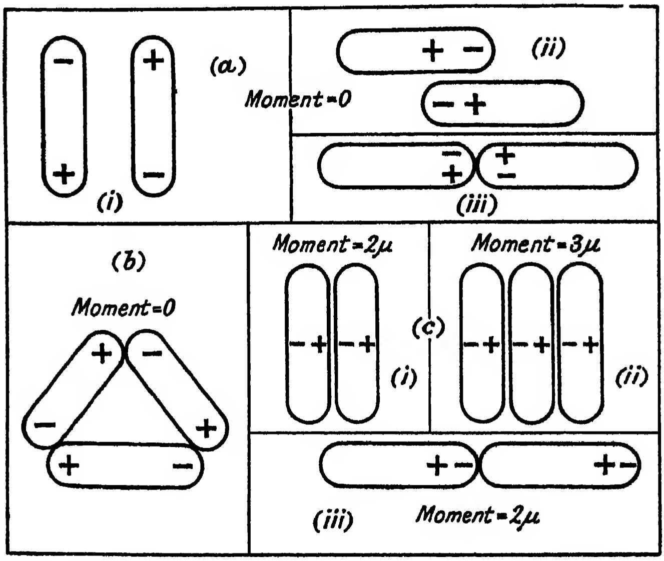


FIGURE LXXXIV.—MOLECULAR DIPOLES IN ASSOCIATION. Here a(i), a(ii), a(iii), and b designate cases where dipoles combine so as to give zero resultant moment, whilst in c(i), c(ii) and c(iii) they reinforce each other.

Gross[214] has examined the values of P and R ($=P_E$) for a number of *halogenated organic liquids*, and finds that for compounds of similar type P is almost independent of the halogen present: thus, for C_6H_5X, when X = F, P = 61·4, Cl 62·0, Br 62·7, I 60·7. In any series of corresponding compounds, from chloride to iodide, R increases and μ decreases, the effects practically compensating each other, the rise in electron polarization together with falling orientation polarization giving nearly constant total polarization. Further, P is always less than P_∞, the total polarization calculated by the dilute solution extrapolation method, where association is absent, the reduction $P - P_\infty$ being attributed to dipole association of types (a) and (b). In accordance with this, it is found that this reduction is least for iodo-compounds, in agreement with anticipation, since here the μ's are smallest, and the dipole association may be expected to be least. These results are illustrated by the following figures for the *ortho-di-halogenated benzenes* :—

	P	R	μ	P_∞
Ortho-dichlorobenzene ..	84·2	36·0	2·00	119
Ortho-dibromobenzene	82·1	41·8	1·52	90
Ortho-diiodobenzene ...	78·4	51·9	1·32	89

Somewhat similar results have been found for the *hydrogen halide gases* by Clark.[215] The P_E values increase, and the P_0 values decrease from HF to HI, but not in such a way as to cause compensation in the total polarization P, as in the liquids studied by Gross.

Girard[216] has studied the dipole association of pure liquids of the alcohol type. The liquids fall into two groups, according as the association is of types (a) and (b), or type (c), which may be termed non-polar and polar association respectively. *Tertiary alcohols* form non-polar association complexes, as do primary alcohols. It can be foreseen that, in these cases, as the temperature is raised, the complexes will tend to break up and so set free new dipoles, which may partially or even completely compensate for the effect of the increase in thermal agitation in decreasing the polarization of the medium. The ϵ/T curves may be interpreted on this basis. In this connection, it may be noted that Smyth and Rogers[217] found an increase in ϵ with rising T for *acetic* and *butyric acids*. The Debye theory requires falling ϵ with increasing T, so the discrepancy may safely be attributed to the effect of association. Girard and Abadie[218] found examples of the formation of polar complexes amongst the *polyhydric alcohols*, the moments being given very approximately by $1{\cdot}6\sqrt{n}$, where n is the number of hydroxyl groups. The absorption and dispersion of the polyhydric alcohols has been examined with a view to throwing light on the problem of their association : it is found, for instance, that the formation of the polar complexes gives rise to discontinuities in the dispersion (ϵ/λ) curves.

Early observations on the influence of field strength on the dielectric constants of polar liquids had indicated small decreases in ϵ with increasing field (see this Vol. : 27Ac). More recently, Malsch[219] found definite effects, $\Delta\epsilon/\epsilon$ being linear with the square of field strength. The deviations from the requirements of the Debye theory were found to be greatest for liquids having the largest ϵ's, and the departures might therefore be attributed to association. It was also found that the shift in the region of anomalous dispersion was greater, the larger the value of ϵ and the greater the degree of association.

Concerning the association of inorganic compounds, it has been observed (this Vol. : 36A) that Zahn[220] found decreasing moment in the series from *hydrogen chloride* to *hydrogen iodide*. Although some authors have held contrary views, it has been argued by Clark[215] that *hydrogen fluoride* will possess the highest moment in the series, in accordance with the known capacity of the gas to associate, revealed by independent experiments.

(B) **Liquid Mixtures.** It may first be noted, as already pointed out, that moments deduced from measurements in solution by extrapolation to infinite dilution take no account of association, since the aggregation of molecules decreases with increasing dilution.

The curves marked III in Figures LXXXI, LXXXII and LXXXIII may now be considered in relation to the theory of dipole association advanced in the above sub-section A. Considering Figure LXXXI for *benzene-ether* mixtures, the constancy of the contribution of ether to the total polarization indicates that ether is unassociated in benzene. In Figure LXXXII, a progressive fall in the contribution made by *chlorobenzene in benzene* is observed, a similar curve having been obtained for *nitrobenzene in benzene.* Here the natural dipole moments tend to raise the orientation polarization, but resulting association (increasing with concentration) tends to lower it, if the association is of type (a) in Figure LXXXIV. Figure LXXXIII shows the case of *alcohol in benzene*, where a maximum is observed for the contribution of the alcohol to the total polarization with changing concentration. Here it has been supposed that in the more dilute solutions of alcohol, the increasing contribution of alcohol may be explained by increasing association, probably in pairs, of type (c); after a certain critical concentration, triple molecules of type (b) may increasingly make their appearance, with attendant reduction of effective moment. Lange[221] has studied numerous cases, and found *nitrobenzene* and *pyridine in benzene* to give curves of the type of Figure LXXXII, whilst *propyl alcohol, n-butyl-alcohol* and *isobutylalcohol* gave maxima like that in Figure LXXXIII. *Isoamylalcohol* was exceptional in giving a curve with two maxima. This was considered to be due to the superposition of two curves, the alcohol being a mixture of two isomeric forms.

The influence of temperature was studied by Lange,[221] for *nitrobenzene in benzene* (24°, 45° and 65°C.) and for *propyl alcohol in benzene* (24°, 41° and 70°C.). Debye's formula [equation (18) of cap. XI] suggests that polarization decreases with increasing temperature, and it was found that for a given concentration the contribution P_2 of the substance dissolved in benzene to the total polarization of the mixture diminished with increasing temperature. The magnitude of the change did not obey the formula, which was deduced without taking account of association. If the formula were followed, multiplication of P_2 for absolute temperature T by the factor $T/273$ should lead to a constant amount for a given concentration; deviations from this give a measure of the effect of association. The temperature coefficient α of $P_2T/273$ was calculated for different concentrations according to the formula

$$\alpha = \frac{\left(\frac{P_2T}{273}\right)_{T_2} - \left(\frac{P_2T}{273}\right)_{T_1}}{T_2 - T_1} \quad \ldots\ldots\ldots\ldots \quad (15)$$

using $T_1 = 273 + 24$ and $T_2 = 273 + 65$ for nitrobenzene, and $T_1 = 273 + 24$ and $T_2 = 273 + 70$ for propyl alcohol in benzene. It was thus found that the rising portions of the P_2 curves corresponded to negative values of a, so that the mean moment decreased with rising temperature. Conversely, the falling portions of the P_2 curves yielded a positive temperature coefficient, or an increase of mean dipole moment with temperature. In all cases, increasing temperature will tend to lessen association, but if rising portions of P_2 curves (as in the first part of curve III of Figure LXXXIII) correspond to association of type (c), and falling portions to association of types (a) or (b), it follows that the effect on moment will be opposite in the two cases. A little reflection shows that the effects work according to anticipation. Repression of dipole association of type (c) (rising portions of curves) caused by increasing temperature will decrease the mean moment, since association of this type tends to raise it; whilst repression of association of type (a) or (b) will tend to raise the mean moment and thus act in the opposite way, in agreement with observation. The results may be summarized as follows :—

Portion of P_2 Curve	Association Type	Effect of Temperature	Effect on Moment	Effect on a
Falling	(a) or (b)	Repression of (a) or (b)	Increase	Positive
Rising	(c)	Repression of (c)	Decrease	Negative

The effect of various factors in decreasing dipole association may be summarized as follows: (1) Increasing symmetry of the molecular group (association of types (a) and (b)); (2) Increasing size of molecule (in homologous series); (3) Increasing temperature; (4) Decreasing concentration in solution.

Further results on *nitrobenzene* have been recorded as follows. Wehrle[222] studied mixtures in non-polar *benzene*, and polar *ether* and *chlorobenzene*. It was found that association may occur not only between molecules of the same but also of different substances, so long as both are polar. Solutions in *benzene* and *carbon tetrachloride* have been examined in respect of their polarization, the evidence pointing to the electrical origin of the association of polar molecules.[223] Piekara[224] has discussed the molecular polarization in *hexane*, and has calculated the degrees of association at 5°, 15° and 25°C. On the other hand, van Arkel and Snoek[225] hold that nitrobenzene is unassociated in *toluene*, *benzene*, *hexane* and *carbon bisulphide*. The argument is based upon earlier work, as a result of which it appeared that nitrobenzene was a non-associating molecule, and upon the use of the modified Debye formula suggested by the authors (see this Vol.: 37D). The constant c in this formula depends upon the dipole moment involved, and is characteristic of a given molecule and independent of the solvent, unless association occurs. For nitrobenzene, $c = 1{\cdot}33$ in the four solvents, and zero association is deduced. This conclusion would leave the experimental observations of many earlier workers unexplained, and it seems impossible to accept it as final.

According to van Arkel and Snoek,[225] *benzonitrile* is unassociated in *benzene*, but associated in *hexane*. This is attributed to benzene molecules having higher external fields than those of hexane. The association falls in the series CH_3CN, CH_2ClCN, CCl_3CN, in the direction of decreasing dipole moment, and is greater in hexane than in benzene in any given case.

Graffunder and Heymann[226] took the departure from linearity of P_2 curves as evidence of changing degrees of association of *acetone* or *alcohol* in *chloroform* or *carbon tetrachloride* with changing concentration. For many other liquid mixtures linear relations were found. A small increase of dipole moment of dilute solutions of *oximes in benzene* has been attributed to association.[188] The association of *chlorobenzene* and *bromobenzene* in *carbon tetrachloride* has been investigated, with respect to changes with concentration and temperature.[227]

Berger[228] has made an attempt to compare conclusions drawn about association in *benzene* from dipole moments with those deduced from measurements of boiling-point elevation The ratio between the observed and the theoretical elevation for many *mono-* and *di-substituted benzenes* could be written in the form $B-Ac$, where A is a measure of association of a given substance. Approximate proportionality between A and μ was observed in many cases · for di-derivatives where the substituent groups had moments of the same sign (*e.g.*, Cl-NO_2) the association decreased from ortho- to para-compounds, and when the signs were unlike (*e.g.*, NO_2-NH_2) the converse was true (see Table XLIX).

According to the distribution measurements on *phenol* between *benzene* and *water* of Philip and Clark,[229] phenol is increasingly associated as its concentration in benzene increases, in agreement with independent evidence. On the other hand, the polarization measurements of Williams and Allgeier[230] show constant P_2 values up to about 40% phenol in benzene, a result which has been confirmed by Donle,[43] over a less wide region of concentration. No explanation appears to have been offered for these and kindred anomalies.

It has been found by Smyth and Engel[231] that Langmuir's theory of molecular surface energies in predicting the partial vapour pressures of binary mixtures of liquids breaks down if one constituent (an alcohol) has dipole moment. The authors have attempted to explain the observed divergencies in terms of interactions between dipoles.

The formation of a compound between *hydrogen chloride* and *ethyl alcohol* has been suggested to explain the relatively high polarization of the mixtures as compared with that of hydrogen chloride in the gas phase.[232] More recently, Fairbrother[233] has investigated solutions of *hydrogen chloride*, *hydrogen bromide* and *hydrogen iodide* in *benzene* and *carbon tetrachloride* as solvents. The dipole moments are higher than in the gas phase, and this is attributed to an increased ionic condition, under the polarizing influence of the dipoles induced in the solvent molecules by the fields of the solute dipoles. No check, however, has been made upon Zahn's measurements[220] of the dipole moments of the free gases, and confirmation would strengthen the arguments concerning the nature of their solutions in organic solvents.

Fairbrother's result, if confirmed, might be accounted for by combination between solute and solvent perhaps almost equally well as in the explanation adopted. The formation of primary association products of this type is generally linked with considerable chemical reactivity. In many cases of ordinary reaction, it appears that primary associations are first formed, afterwards yielding the normal products of the reaction, as in the various decompositions of *formic acid* under the influence of catalysts.[234] The intermediate compounds are seldom capable of isolation.

(C) **Theories of Dipole Association.** Various types of association processes may be distinguished, with Ebert,[213] as follows:-—

(1) *Association between ions*; as in ionic crystals, where the linkages are "many-sided"; and in salt vapours, where they are "one-sided";

(2) *Association between ions and dipoles* (co-ordination compounds);

(3) *Association between dipoles* (molecular aggregates);

(4) *Association between dipoles and quadrupoles*;[3]

(5) *Association between quadrupoles.*

Associated ion pairs lead to "salt dipoles," as in NaCl vapour; or possibly to "salt quadrupoles," as in the vapour of Hg_2Cl_2. Walden[235] found, in conformity with this, that the dielectric constants of three organic solvents were raised by the addition of a salt of a quarternary ammonium base (this Vol.: 27D). The interaction between ions and dipoles seems to provide an explanation of the co-ordination compounds,[236] the "solvation" of ions, and, in particular, of the formation of ion hydrates and ammoniates.[237] The co-ordinating atom need not be ionic, however, as in the compounds $A(H_2O)_6$, $S(NH_3)_6$, $Ca(NH_3)_6$, $Ni(CO)_4$ and $Mo(CO)_6$. Combination between dipoles of the same kind may be held responsible for molecular association in pure liquids and vapours, and of substances in solution. When the dipoles are unlike, molecular compounds between solute and solvent may be formed, as in the case of HCl and C_2H_5OH. The explanation of slow homogeneous reactions may lie in the intramolecular change of primary associated products.[238] Dipole association is also probably the preliminary and determining factor in many cases of heterogeneous reaction, in being the underlying cause of adsorption (see following Section 41).

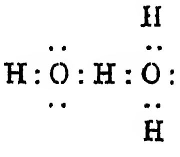
van Arkel and Snoek[37] have classified substances into three classes, with respect to the presence or absence of association, and of variation of dipole moment with temperature:--

(1) *Unassociated with Constant Moment.* Nitrobenzene, iodobenzene, bromobenzene, butyl halides and ethyl acetate are placed in this group.

(2) *Unassociated with Variable Moment* (a), and *Weakly Associated with Constant Moment* (b). An example of (2a) is found in ethylene dibromide. (2b) is represented by ethyl acetate in organic solvents; its association increases from solution in benzene to carbon tetrachloride, and from carbon tetrachloride to hexane.

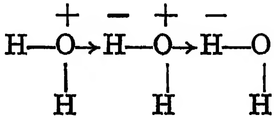
(3) *Strong Association.* Examples are provided by the alcohols and acids in solution. The relations are generally very complex.

The tendency of hydroxylated substances to associate is well known from independent evidence. In the case of *water*, Latimer and Rodebush[239] suggested that an oxygen atom of one molecule might form a link with the hydrogen atom of another by sharing a pair of electrons, the hydrogen atom becoming effectively bivalent, as follows:-



$$\begin{array}{cccccccc} & & & & & & \mathrm{H} & \\ & & \cdot\cdot & & & & \cdot\cdot & \\ \mathrm{H} & : & \mathrm{O} & : & \mathrm{H} & : & \mathrm{O} & : \\ & & \cdot\cdot & & & & \cdot\cdot & \\ & & & & & & \mathrm{H} & \end{array}$$

where the double dots signify pairs of electrons. A similar explanation may be used for *alcohols* and *phenols*. Sidgwick[240] suggested the terms "donor" and "acceptor" for atoms giving or receiving pairs of electrons respectively. The structure of associated water may then be represented as follows, the arrows denoting directions of transfer of electrons :—



$$H—\underset{\underset{H}{|}}{\overset{+}{O}}\rightarrow\overset{-}{H}—\underset{\underset{H}{|}}{\overset{+}{O}}\rightarrow\overset{-}{H}—\underset{\underset{H}{|}}{O}$$

Compounds containing an amine group also show some tendency to associate. The $P_A + P_O$ values for a series of *amines* are given by Ebert[218] as follows: HNH_2, 15·9; $C_2H_5NH_2$, 26·4; $(C_2H_5)_2NH$, 23·3; $(C_2H_5)_3N$, 24·5. Here association of type (a) lowers the dipole moment of ammonia.

The hypothesis of Sidgwick has been criticized as a result of experiments on molecular refraction. Smyth, Engel and Wilson[241] argued that the presence of a semi-polar bond (of the donor-acceptor type) should cause a diminution in molecular refraction of from 0·2 to 0·5 unit. It was found that the refraction of alcohol was independent of its concentration in heptane, whilst association would be expected to increase and refraction decrease with increasing concentration. Moreover, it was observed that the refraction of alkyl halides dissolved in heptane varied with temperature to about the same extent as an alcohol in heptane. Since alkyl halides cannot co-ordinate in the donor-acceptor way, the result was regarded as evidence against the Sidgwick hypothesis of co-ordination. Smyth and co-workers therefore assume the association to involve merely an orientation brought about by the strong forces between the dipoles. Similar views have been expressed by Martin and collaborators,[242] who observed no change of refractivity with concentration for phenol-benzene and benzyl alcohol-benzene mixtures. This argument against the semi-polar bond theory of co-ordination of alcohols and phenols is supported by the earlier observation of Fajans and Joos of the lowering of refraction of the oxygen anion by successive laying-on of protons (see this Vol.: 34Db).

Rolinski[243] has attempted to calculate degrees of association from dipole measurements on solutions. Following Debye, he attributed deviations from additivity requirements of liquid mixtures to association. It was found that dipole-free liquids (benzene, carbon bisulphide, carbon tetrachloride) showed no departures from additivity in mixture with each other, and the molecular polarization was independent of concentration. Mixtures in which one component (benzene-ether) possessed intrinsic moment, and those in which both components (chlorobenzene-quinoline) had moment, showed a fall in molecular polarization with increasing concentration, indicating increasing association of types (a) or (b). The equation of Debye was rewritten in the form

$$P = \frac{4}{3}\pi N\alpha + \frac{4}{3}\pi N_0 \frac{\mu^2}{3kT} \quad \dots\dots\dots\dots\dots\dots \quad (16)$$

where the degree of association α is given by $1 - (N_0/N)$, N being the total, and N_0 the unassociated number of molecules present at a given dilution. It was found that, for corresponding molecular concentrations, the association increased for the following substances in the order ethyl ether→chlorobenzene→pyridine→quinoline→nitrobenzene, which order is the same as that of ascending dipole moments of the unassociated molecules deduced by extrapolation to infinite dilution of solutions. Wolfke[214] has extended these calculations by theoretical treatment on the basis of the Einstein exponential probability law of distribution of associated and unassociated molecules. In this way, good general agreement was obtained between degrees of dissociation calculated theoretically and those deduced from experiment by Rolinski's method. More recently,[245] the calculation has been extended to cases involving association of type (c), where increased moment occurs in certain concentrations. Curves showing maxima, in agreement with the experiments of Lange[221] on alcohols in benzene were reproduced in the theoretical analysis. Sakurada[246] has further derived a simple relation between orientation polarization and the concentration of solution on the basis of the Law of Mass Action, whereby the degree of dissociation may be found. Comparison with the experimental data of Rolinski, Williams and Lange on chlorobenzene, chloroform, methyl acetate, ethyl acetate and nitrobenzene in non-polar solutes gave satisfactory agreement. It was found that nitrobenzene gave triple, and the other molecules double complexes of zero moment. A satisfactory beginning has thus been made in allowing for the influence of association of different types.

41. Dipoles and Adsorption

No attempt is made in the present section to deal with the general theory of adsorption. A brief survey is provided of the suggested mechanism of the process in terms of polarization phenomena.

Polanyi[247] considered the data of Titoff[248] on the adsorption of *carbon dioxide by charcoal,* and concluded that they might be accounted for by the mutual orientation of the magnetic and electric fields of adsorbent and adsorbed substance, in such a way as to cause attraction and consequent close approach of the two kinds of molecule. It is further supposed that subsequent deformation between molecules in contact on the adsorbent surface may occur in such a way as to set up induced dipoles, enabling opposite poles to approach each other more closely. Mukherjee[249] considered the origin of the charge of the adsorbent and the relation between charge and concentration of adsorbed substance. It was concluded that the first interaction is of a chemical nature, followed by electrical adsorption with the formation of an electrical double layer. Kar and Ganguli[250] have argued that there exists no essential difference between electrical and chemical adsorption, the theory being worked out on this basis. Eucken[251] earlier expressed similar views, and considered data on the adsorption of *argon by charcoal,* where it was unlikely that any chemical forces could operate, and where the effect seemed to be due to the same forces as are concerned in the condensation of argon to the liquid state. These forces would be such as are found in polarization, and would operate over small distances only, compared with molecular dimensions (see Vol. I: Figure XXXIII). Lorenz and Landé[252] concluded that adsorption results might be used to calculate the dipole moments of adsorbed substances, but so far this hope has not been fulfilled. The studies of Frumkin[253] and Guyot[254] indicate that the interface values of moment are always too low. Frumkin and Williams[255] have concluded that some factor has been left out of account in making the calculation.

Lorenz and Landé[252] found that the observed heats of adsorption might be accounted for, so far as orders of magnitude are concerned, on the basis of a dipole molecule held to the adsorbent surface by attraction between itself and a mirror-image induced dipole within the surface. The potential energy of a dipole in the field of its electrical image is $J = -\mu^2(1 + \cos^2\theta)/r^3$, where r is the distance between the dipole centres and θ is the angle of inclination of the dipoles to the normal at the adsorbing surface. (This result may be easily obtained from the formula given at the end of Section 3 of the Appendix to Chapter XIV, by putting $\mu = m_1 = m_2$, and $\theta_1 = \theta$, $\theta_2 = 180° - \theta$). Lorenz and Landé only considered single films, but Bradley[256] showed that thicker films might be possible (see Vol. 1: 33Cf, end).

The work of Magnus[257,259,260] has done much to extend the electrical theory of the origin of adsorptive cohesion. In the case of carbon dioxide, which has zero moment, adsorbed on charcoal, it was assumed that an induced dipole was set up by deformation, whereby the C atom was attracted nearer to the surface than the two O's, a similar dipole being set up within the surface.[257] It thus became possible to extend the polarization theory to non-polar molecules. Magnus also discussed heat of adsorption, which was found to fall with increasing pressure of carbon dioxide. This was accounted for by inequalities in the surface, molecules being more firmly bound at certain points than at others. Herzfeld[258] considered adsorption heats in further detail. It was found that these might either decrease (as in the case considered by Magnus) or increase with increasing amount of gas adsorbed on a solid surface. Decreasing adsorption heats with increasing concentration of adsorbed substance could be readily accounted for on the basis of inequalities in the surface, the higher points having smaller affinity for gas molecules. Hence the spots on the surface having higher affinity will adsorb the first part of the gas, and give up larger amounts of heat than in later stages of the process. This explanation will not account for cases where the adsorption heat increases with increasing covering of the adsorbent surface, and Herzfeld introduces the conception of increasing interaction of neighbouring dipoles, with heat evolution, in explanation. The number of places on the surface where two or more adsorbed molecules lie close together will increase more rapidly than the amount of gas adsorbed in places with isolated molecules, according to this suggestion. Examples are provided by *hydrogen* or *oxygen* on the surfaces of *sodium chloride* or *fluorspar*. The factor which determines which of these opposed processes shall prevail in a given case is apparently unspecified.

Magnus[259] worked out the theory of the adsorption of polar water vapour and non-polar carbon dioxide as two-dimensional gas phases. Attention was also paid to the variation of adsorption heats with temperature, as observed below. In cases where the adsorbed gas molecule has zero moment, and an induced dipole is set up (*e.g.*, carbon dioxide), the layers may be expected to be monomolecular. When dipole moment is present, thicker layers may be formed, with increased adsorption: thus SO_2 is more strongly adsorbed than CO_2, and NH_3 and OH_2 than CH_4, other things being equal. At low surface concentrations, the molecules can move freely about: they also vibrate perpendicular to the surface. Some molecules having high enough energies can escape, whilst others arriving are retained. In this region of concentration, therefore, the concentrations in the adsorbed and gaseous phases are proportional to each other (*cf.* Henry's Law), and the heat of adsorption is independent of concentration. At higher concentrations, the relations are more complex, due to interactions between the adsorbed molecules. On raising the temperature, the amplitude of vibrations perpendicular to the surface increases, the mean distance from the surface increases, and the attraction between the dipoles of the gas molecules and their mirror-images decreases, so that the heat of adsorption falls. This theory may perhaps be the forerunner of a more rigid explanation. A beginning has been made on the basis of the wave-mechanics.[261,262]

Inequalities in an adsorbent in different parts of its surface may account for the *activation of charcoal*[263] Activation may be carried out by air, steam, and chemical reagents (zinc chloride, phosphoric acid and ferments), and it is suggested that the surface carbon atoms have one free valency capable of anchoring a vapour molecule, and that activation may cause pitting and extension of the number of available points of attachment. If the activation process be carried too far, deactivation may set in, as the surface pits become wider.

Perrin[264] expressed the view that the stability of *electrically-dispersed metal systems* depended directly upon the dielectric constants of the dispersion media. Svedberg[265] noted exceptions to this, finding that *platinum sols* in *methyl and ethyl alcohols* were unstable, although the dielectric constants of the alcohols are relatively high. Wo. Ostwald[266] reported that the *swelling of rubber* was greater in liquids of lower dielectric constant. It has been found that a better interpretation of the stabilities of metalic organosols can be derived in terms of the orientation polarizations (dipole moments) of the dispersion media.[267] Burton[268] found that the particles of dispersed metal carried charges in certain media, the charges apparently arising from interaction between the particles and the medium. It would be anticipated that media of higher dipole moment would yield more stable groups in the neighbourhood of charged particles, the solvent dipoles being orientated towards them: thus media of high intrinsic moment would produce more stable sols whose coagulation and precipitation would be prevented or at least delayed. Errera[269] prepared sols of *platinum, mercury and copper sulphides* in various media by chemical methods, and found the addition of substances having a lower dielectric constant than the solvent to cause precipitation, and conversely; exactly opposite to the effect mentioned above. According to Wo. Ostwald,[266] this may be attributed to the presence of ions as well as dipoles in the sheaths surrounding these colloid particles prepared by chemical means. Thus an HgS-alcohol sol may be coagulated and precipitated by addition of benzene. The sheath surrounding the micelle and responsible for its stabilization contains ions and alcohol dipoles. Benzene raises the polarization of the alcohol up to a maximum at a concentration of about 33% (curve B in Figure LXXXIII). The interaction between the ions and the alcohol dipoles leads to the destruction of the ion absorption layer with consequent coagulation of particles and

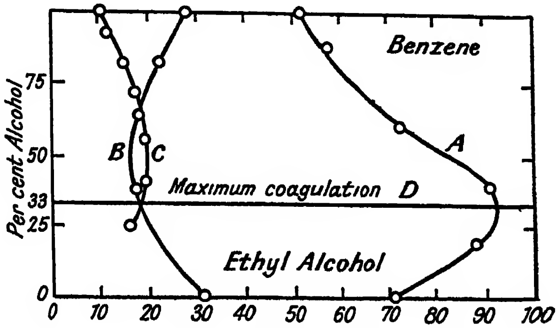


FIGURE LXXXV.—RELATION BETWEEN POLARIZATION OF BENZENE-ETHYL ALCOHOL MIXTURES, SOLUBILITY OF PICRIC ACID AND ITS ADSORPTION ON CHARCOAL IN THEM. A is reproduced from curve III of Figure LXXXIII, B shows the adsorption of picric acid by charcoal in different mixtures, C represents the solubility relations, D shows the optimum concentration for coagulation

precipitation. Errera found that the optimum concentration for coagulation corresponded to that of benzene-alcohol mixtures having the highest total polarization. Angelescu and Comănescu[270] observed that the adsorption of *picric acid by charcoal* reached a minimum in benzene-alcohol mixtures of this concentration.

A close connection exists between solubility and adsorption.[271] The more soluble a substance is in a given medium, the less easily is it adsorbed from the medium.[272,273] Curve C in Figure LXXXV is drawn from the measurements of Angelescu and Dumitrescu,[274] and shows the solubility of picric acid in alcohol-benzene mixtures. In accordance with the theory, the minimum of curve B, showing adsorption, roughly corresponds to the maximum of curve C, whilst both are not very far removed from the concentration of alcohol in benzene containing 33% alcohol having maximum dipole moment of alcohol and maximum coagulating efficiency. This result seems to illustrate the relations between adsorption, solubility and polarization particularly well.

Hermann and Boye[275] have carried the above researches a little further, by examining the often complex behaviour of liquid mixtures of different types in respect of influence of adsorption of substances by charcoal. In general, linear adsorption-concentration curves are obtained in the case of picric acid when both components are non-polar (benzene-carbon tetrachloride) or when one component only is polar (toluene-carbon tetrachloride) so long as no interaction occurs between the two liquids. Curved adsorption curves occur when one component is polar and is affected by the other (benzene-nitrobenzene) and when both components are polar (water-alcohol, chloroform-alcohol, etc.). The general relations between solubility and adsorbability are confirmed. In comparing different substances in respect of the dipole moments of the media, it is best to compare substances of related constitution, for example, an homologous series of alcohols, when it is found that the solubility of an ion-yielding substance like picric acid increases with increasing deformability of the alcohol, whilst the adsorption diminishes. The experimental method, using picric or benzoic acids, was to centrifuge a mixture and titrate the residual acid in the medium.

According to the theory of Debye and Huckel, an ion in solution in a polar solvent tends to surround itself with an " ionic atmosphere " of orientated solvent dipoles. This theory is found to throw light on the problem of the conductivity of more concentrated solutions of electrolytes. The building-up of the dipole distribution involves a time factor, which in turn causes a " braking " effect on the ion and alters its conductivity.

The adsorption of *potassium chloride* and *iodide* and *sodium chloride* from aqueous solutions on negatively-charged *barium sulphate* follows the same changes with concentration as on the positively-charged substance.[276] It may be assumed that the actions are similar, the positive ions being attracted to the negative surface, and *vice versa.*

Bergmann[277] has found that the blue colour developed on addition of *iodine* to *starch solutions* is due to adsorption.

Adsorption is particularly important from the chemical standpoint in the study of surface catalysis. Three factors may be taken into account: (1) the extent of the surface; (2) the capacity of the solid to adsorb the reactants; (3) the ability to form adsorption complexes. When two gases are adsorbed together, their molecules are brought into such close contact that the speed of possible reaction between them may be greatly accelerated, as in many familiar instances.[278] Recent studies include the investigation of the electrical condition of hot metallic surfaces during the adsorption of gases, the results being discussed in relation to catalytic activity.[279,280]

The terms " adatom " and " adion " have been suggested by Becker[281] to denote an adsorbed atom and ion respectively.

Matter in the adsorbed phase must be regarded as being in a different, and generally more active, state than ordinary. The explanation put forward of this behaviour on the basis of polarization effects has yielded good general agreement with experiment.

42. Dipole Moments of Inorganic Compounds

(A) **The Hydrogen Halides, Hydrogen Cyanide and Cyanogen.** Zahn[220] determined the dipole moments of the *hydrogen halide gases* by the method of temperature variation of dielectric constant, as follows: HCl 1·03, HBr 0·78, HI 0·38. van Vleck (see [283]) calculated the moments from the total polarizations at N.T.P. as measured by Zahn, and the optical polarizations for infinite wave-length, deduced from the measurements of Cuthbertson and Cuthbertson, as follows: HCl 1·06, HBr 0·80, HI 0·41, in substantial agreement with the directly obtained values of Zahn. Since these numbers co-ordinate two sets of independent measurements, they are perhaps the most reliable so far available. Other values have, however, been obtained. For example, Estermann and

Fraser[282] found $\mu = 1 \cdot 95$ for HCl by the molecular ray method, though no great accuracy is claimed, whilst Fairbrother[283] found higher values by the solution method: (in benzene) HCl 1·26, HBr 1·01, HI 0·58; (in carbon tetrachloride) HBr 0·96, HI 0·50, whilst in the solvents ethyl bromide and ethylene dibromide the respective practically normal values of 1·02 and 0·97 were obtained for HCl.[283]

The internuclear distance r_e for HCl deduced from band spectra is 1·272 Å.U.: if, now, the dipole distance d had been equal to this, the moment would have been $\mu' = er_e = 1 \cdot 272 \times 4 \cdot 77 = 6 \cdot 07$, where e is the electronic charge. This high value compared with experiment leads to the conclusion that HCl behaves as if only 17·5% polar, and that the molecule exhibits considerable deformation, by the proton H^+ entering the negative Cl^- ion (see Table in this Vol.: 34Db). An induced dipole is set up, tending to lessen the natural dipole, since it acts in the opposite sense. The effect of the induction will be to cause diminishing moment in the series from HCl to HI, since the polarizability of the negative ion increases from Cl^- to I^-. Debye has deduced the relation

$$\mu = \mu' \left(1 - \frac{\alpha'}{r_e^3}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

where α' is the " apparent polarizability " of the negative ion (see [284]).

The apparent polarizability P' may be found by using $P' = 4\pi N\alpha/3$, obtaining α' from (17), when it is found that the values for HCl and HBr agree very closely with the molecular refractions of argon and krypton respectively, the inert gases having the same numbers of outer electrons: thus for HCl, $P' = 4 \cdot 31$, R(argon) $= 4 \cdot 23$; HBr, $P' = 6 \cdot 27$, R(krypton) $= 6 \cdot 42$. Born and Heisenberg[285] gave the polarizabilities α of the negative ions, whilst Clark[123] calculated the values α'' which are conformable with the dispersion of refractive indices as measured by Cuthbertson and Cuthbertson. The results indicate that α is too large, and α' too small a measure of the true polarizabilities α''. A simple relation, however, exists between these numbers: the lowering of polarizability of a halide ion by a proton $\alpha - \alpha''$ being in linear relation with Debye's α' according to the expression.[215]

$$\alpha - \alpha'' = 0{\cdot}25\alpha' + 0{\cdot}06 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

from which it appears that *the apparent polarizability* α' *is a measure of this lowering* for each of the four halides. This is shown in the following scheme:

Di-atom	α	α'	α''	
			(expt.)	(calc.)
HF	0·99	(0·40)	(0·80)	0·83
HCl	3·05	1·70	2·56	2·56
HBr	4·17	2·48	3·49	3·49
HI	6·28	4·16	5·18	5·18

The agreement with experiment is observed to be exact, except in the case of HF, where the numbers are somewhat less reliable, being partly deduced from estimates.

A further point of interest arises in connection with the discovery that $\alpha'' \propto r_e^3$, so that *the cube of internuclear distance is a measure of the polarizability of a hydrogen halide.* The relation is $\alpha'' = 1{\cdot}242r_e^3$ [215], and is of virtually the same form as an equation suggested by von Wiśniewski,[286] who wrongly assumed the applicability of Maxwell's rule to the polar hydrogen halides. The above result, however, turns out to be independent of this assumption. A similar relation has also been used by Bergmann and Engel[287] in deducing interatomic distances of inorganic halides of more complex character (see Section 42K below), and was applied to the hydrogen halides, but with not very good success. Further analysis of these results might be extremely fruitful.

Mulliken[288] has pointed out that dipole moments as normally given refer to equilibrium internuclear separations. Since the nuclei are in vibration, the dipole moment must be continually changing. A study is made of the variation of μ with internuclear distance for HCl, HBr and HI and other cases.

An attempt has been made to find a relation between the solubility of HCl in different organic solvents.[289] Although a tendency towards increasing solubility with increasing dielectric constant of the medium is found, it is clear that the parallelism is not exact. Some other factor enters in, and it is suggested that this may be associated with the discontinuous nature of the solution in the neighbourhood of solute molecules.

Some discussion has taken place about the most probable dipole moment of HF. According to the quantum-mechanical calculation of Kirkwood,[290] μ(HF) is less than μ(HCl), and Smyth and McAlpine[57] have adopted the provisional value of 0·8 on this basis. Smallwood[291] has obtained the higher figure 2·0 by extrapolation, whilst Clark[123] has found the value 1·58 between these extremes. Smallwood's extrapolation is liable to considerable uncertainty: Clark's estimate is also open to question, since it is based on the assumption that the apparent polarizability of HF is equal to the molecular refraction of neon, and it is somewhat uncertain whether Debye's principle may be extended to this case. However this may be, the weight of evidence seems to be definitely in favour of the idea that HF is the most polar molecule in the group of hydrogen halides (see discussion in [215]).

The dipole moment of a compound HX is generally less than that of RX, where R is an alkyl group. Thus we may expect the moment of HCN to be less than that of methyl cyanide 3·16 (this Vol.: 38F): according to a recent measurement of Smyth and McAlpine, it is 2·932 for *hydrogen cyanide* gas. Earlier measurements yielded lower values.[43] *Cyanogen* gas, examined by Braune and Asche,[293] gave the small, though appreciable, moment of 0·3. The fall in moment between HCN and C_2N_2 must be attributed to increasing symmetry.

(B) **Carbon Monoxide and Derivatives.** Early measurements[43] indicated that *carbon monoxide* possessed a small moment, about 0·10, which exactly agrees with a more recent result of Rao and Ramaswamy.[294] The structure of the molecule has been much discussed. Early evidence, based on the Heitler-London theory of molecule formation, suggested a double bond for CO, in conformity with its known tendency to form addition compounds such as $COCl_2$. The characteristic frequency derived from the Raman Effect, however, suggested a triple link, in agreement with the fact that CO and N_2 are assigned similar electron configurations, the bond in N_2 being certainly triple. Hammick, New, Sidgwick and Sutton[157] suggested that the third linkage was semi-polar, both electrons for it coming from the oxygen atom. Lessheim and Samuel[295] urged that the pair of electrons provided by the same atom should not be counted as taking part in the link, which was therefore considered to be double. Pauling and Sherman[297] have adduced evidence that the heats of formation of many molecules are less than those calculated for any simple structures, and have attributed this to the presence of resonance mixtures of different forms. It was found that CO corresponded to a mixture of $C^- \equiv O^+$ and $C = O$,[298] to which Mulliken[288] has added a component $C^+ - O^-$. Sutton[299] has reached similar conclusions on the basis of dipole moment calculations: it is found that $C = O$ and $C \equiv O$ correspond to moments of $-2{\cdot}7$ and $1{\cdot}4$ respectively, from which further support for the theory of an equilibrium mixture is derived. The case in favour of a resonance mixture in CO is thus rather strongly upheld. It may be further argued that CO behaves as if consisting of molecules in which a triple linkage, more polar than that of N_2, is found. Evidence derived from bond constants and mean restoring forces of molecules of similar type lends some weight to this view.[300]

Phosgene[292] has a much higher moment than CO, doubtless due to the additional asymmetry introduced by the addition of two C–Cl moments. *Iron pentacarbonyl*[287] is assigned the moment 0·64. It is suggested that in $Fe(CO)_5$ one CO group is attached to Fe differently from the other four, as in the structure of $SbCl_5$ (see Section 42K below). This structure seems to be supported by the chemical behaviour of iron pentacarbonyl.

(C) **Water and Hydrogen Peroxide.** An asymmetric model of the water molecule was suggested, prior to the theory of dipoles, on thermal grounds. Boltzmann found that the molecule possessed energy of rotation in three directions at right angles. Nernst[301] measured the molecular heat of water vapour at constant pressure at low temperature, and found $C_p = 7{\cdot}94 = 8R/2$, which gives the molecular heat at constant volume $C_v = C_p - R = 6R/2 = 5{\cdot}95$ This corresponds to six degrees of freedom, three of which are of translation in three directions at right angles. If the remaining three degrees of freedom are of rotation, there must be three axes of rotation at right angles in space, which would not be provided by a linear model. Further, the ratio $C_p/C_v = 1{\cdot}33$, whilst a linear symmetrical model requires 1·4.

Vorländer (dissertation with Weber, 1914)[302] suggested a triangular model for the water molecule, having the (tetrahedral) angle 109°, as an outcome of a study of the properties of certain organic liquid crystals.

Rubens and Hettner,[303] in the course of a study of the long-wave absorption spectrum of water vapour, suggested the model of an isosceles triangle. It was found that the molecule possessed three degrees of freedom of rotation in agreement with the thermal evidence , there would therefore be three axes of rotation and three moments of inertia This was confirmed by Eucken[304] from the separation of lines in the infra-red absorption band, the following values being found . 3·20, 2·25 and $0{\cdot}975 \times 10^{-40}$. More recent estimates are 2·955, 1·907 and $1{\cdot}09 \times 10^{-40}$ [305] The three axes at right angles are shown diagrammatically in Figure LXXXVI.

Mecke,[305] after a recent careful analysis of the vibration-rotation bands of water vapour, has adopted the triangular model, with an angle of about 104° between the two oxygen valency directions. This seems to be the best estimate at present available.

Other estimates of the apical angle of water may be briefly noted: Reis[306] 90°; Cuy[307] 109°, Wolf[116] 110°, Piccard[308] 120°. Landé[309] and Hund[310] also found triangular models by calculation. The treatment of Debye[311] is given in the Appendix to Chapter XIV (Section (4)). The method of calculation is of more interest than the actual result (64°) This may be compared with the more recent estimate of 134°,[185] a value nearly twice as great. The nearest distances are O–H 0·972, H–H 1·516, for an angle 102° 30′.[305]

A mean value of the dipole moment of water vapour may be taken as 1·85[43] The fall in the dielectric constant of water on freezing, from 80 to 3·2, may be associated with partial loss of rotation of the dipole molecule on solidification According to Smyth and Hitchcock,[312] *ice* behaves as a very viscous liquid, and shows dipole rotation. Other cases of changes in dielectric constant on freezing are discussed in this Vol.: 28B.

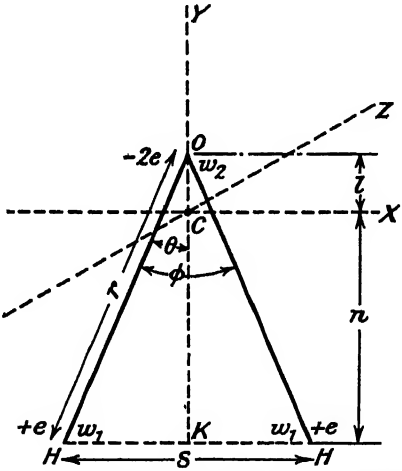


FIGURE LXXXVI —STRUCTURE OF THE WATER MOLECULE (Debye)

The dipole moment of *hydrogen peroxide* was found to be 2·13 in dioxane, and 2·06 in ether solution (Linton and Maass[43]). Theilacker[313] adopted the angle 110° for H_2O,[116] and calculated $\mu_{\mathrm{OH}} = \mu_{\mathrm{H_2O}}/2\cos 55°$. Assuming free rotation about the central O–O line, and that the oxygen valency angles were as in water, it was found that $\mu_{\mathrm{H_2O_2}} = \mu_{\mathrm{OH}}\sin 70°\sqrt{2}$ gave good agreement with experiment (for basis of the formula, see [66]) The calculations of Penney and Sutherland,[314] however, suggest an unsymmetrical model of the type HOOH, with different angles between the two O valency directions, and without free rotation about the central linkage. Similar considerations may apply to hydrazine (Section 42H below).

(D) **Hydrogen Sulphide.** The moment is about 1·1.[43] Hund[310] adopted a triangular model as for water. Hampson, Farmer and Sutton[185] find the angle between the S valencies to be 118° in diphenylsulphoxide, and suggest that the angle is probably smaller than this in H_2S.

(E) **Carbon Dioxide.** The small moment of 0·06 found by Zahn has been gradually reduced to zero by later observations.[43] Eucken[315] and Rawlins[316] have considered the X-ray structure of solid CO_2, the molecular heat, and the dipole moment estimates, and conclude that a linear, symmetrical model OCO will best account for the facts, in agreement with independent spectroscopic evidence. The linear form of the molecule in the solid state appears to be preserved on sublimation.

(F) **Nitrogen Oxides.** An early value of the dipole moment of *nitrous oxide* was 0·25: later measurements by Ghosh and Williams gave zero moment.[43] Czerlinsky[317] and Watson, Rao and Ramaswamy[294] find $\mu = 0{\cdot}14$ ($\pm 0{\cdot}02$) and 0·17 respectively. The linear unsymmetrical model NNO may account for the facts, and would explain the relative case of removal of O better than the model NON. Sutton[299] suggests that a resonance mixture of $N \underline{\leftarrow} N = O$ and $N \equiv N \rightarrow O$ may be present.

Nitric Oxide has been assigned 0·07 (approx)[318] and 0·16.[294] The orientation polarization seems to be small, though definite, perhaps associated with the odd number of molecular electrons, and the presence of a single electron bond. It may consist of a mixture of $N = O$ and $N \underline{\leftarrow} O$.[299]

Zahn[319] found the dipole moment of *nitrogen peroxide* to be 0·39 for NO_2 and 0·55 for N_2O_4 molecules, measurements being made on equilibrium mixtures of the two gases. The apparent increase of moment with association seems striking, but no great accuracy is claimed for the numbers, which may represent upper limits only.

(G) **Sulphur Dioxide and Derivatives.** A high moment of the order of 1.6[43] is reported for sulphur dioxide, indicating asymmetric structure. Two semi-polar bonds inclined to each other would appear to account for this result.

Thionyl chloride, $SOCl_2$, and *sulphuryl chloride*, SO_2Cl_2, have been assigned the respective moments 1·38 and 1·64.[320] It is suggested that semi-polar links raise the moments. A rough estimate of the moment of *sulphur chloride*, SCl_2, is 0·56.[320]

(H) **Ammonia and Hydrazine.** The electric moment of *ammonia* gas is about 1·46.[43] Kossel[321] postulated a polar composition of the molecule, $N^{- - -}$ holding three H^+ ions symmetrically in a plane. On the other hand, Huckel[322] regarded the linkages as homopolar, as in the substituted compound NH_2CH_3. Piccard and Dardel,[323] considering the stereochemical result that the four valencies of co-ordinated nitrogen are directed towards the corners of a regular tetrahedron, suggested that even where three valencies of nitrogen only were satisfied, the nitrogen atom might lie outside the plane of the three hydrogen atoms, thus conferring dipole moment. Hund[310] considered a polar structure in which the four ions formed a tetrahedron with three equal side faces. Robertson and Fox[324] argued from the relatively large temperature coefficient of dielectric constant of ammonia that the molecule possessed tetrahedral symmetry, with the nitrogen atom possibly at no very great distance from the plane of hydrogen atoms. The model is shown in Figure XCIV (see Section (5) of the Appendix to Chapter XIV). The height of the pyramid is computed as 0·38, and the nearest distances N–H 1·02 and H–H 1·64 Å.U.[342]

The moment of *hydrazine*, N_2H_4, is found to be 1·84.[13] Although a symmetrical model with free rotation about the central N–N linkage is possible, Penney and Sutherland[314] postulate a skew arrangement as the most stable configuration, as in the case of hydrogen peroxide.

(J) **Phosphine and Arsine.** The moments are found to be 0·55 and 0·15 respectively (Watson[43]). There is decreasing moment from ammonia to arsine with increasing molecular weight, as in the series from HCl to HI and from H_2O to H_2S. It seems reasonable, adopting tetrahedral frameworks, to ascribe increasing flattening to the structures, with decreasing tetrahedral height as the central atom increases in size from NH_3 to AsH_3. The same kind of effect may operate with successive replacement of H by CH_3 in the series from NH_3 to $N(CH_3)_3$.[325]

(K) **The Halogens and Non-hydride Halides.** Williams and Allgeier[230] found the very considerable moment of 1·4 for *iodine* dissolved in benzene, whilst Müller and Sack[326] gave 1·2 for the red solution in the same solvent. The moment is zero when measurements are made on the violet solutions of iodine in hexane and cyclohexane. The moment in benzene appears to be due to polarization of the iodine molecule by the solvent. Some difference of opinion has evidently existed as to whether the free gas halogen molecules have moment or not. Williams and Allgeier quote moments of 0·58 and 0·13 obtained by Smyth in calculation for *bromine* and *chlorine* respectively These numbers apparently refer to the liquid states of the two halogens, and it is extremely doubtful whether they apply to the vapours According to the very careful measurements of Luft[43] on bromine vapour, the moment is zero to within 0·1 The moments of all the halogen gases are presumably zero, in accordance with their symmetrical structure Liquid bromine has been assigned the moment 0·49 [43] Ions may be present in liquid bromine and iodine, as the evidence of electrical conductivity requires (Vol. 1: 20C). The moments of *iodine monochloride* (0·5[43]) and *iodine monobromide* (1·0[43]) suggest the presence of polar and unsymmetrical molecular structure

The moments of *potassium chloride* (6·3) and *iodide* (6·8), and of *sodium iodide* (4·9) have been estimated by the molecular ray method.[327] An error not greater than ±5% may be present

Amongst bivalent halides, the moments of *beryllium chloride* and *bromide* have been found to be zero.[328] The case of SCl_2 is mentioned above

A convenient list of moments of compounds of MX_3 type has been prepared by Smyth.[53] The following shows the leading results in somewhat more extended form :

	F_3	Cl_3			Br_3			I_3	
Solvent	C_6H_6	C_6H_6	CCl_4	CS_2	C_6H_6	CCl_4	CS_2	C_6H_6	CS_2
B	·	0^{328}	$0\ 21^{316}$	·				… ·	·
Al					$5\ 2^{331}$		0^{331}	$2\ 5^{331}$	0^{331}
P	·	$0\ 90^{330}$	$0\ 80^{316}$			$0\ 61^{316}$		·	0^{329}
As	$2\ 05^{329}$	$2\ 15^{330}$	$1\ 97^{287}$			$1\ 66^{336}$	$1\ 60^{330}$		$0\ 96^{330}$
Sb	…	$3\ 75^{330}$ $4\ 11^{336}$		$3\ 12^{329}$	$3\ 28^{329}$		$2\ 47^{330}$	$0\ 4^{328}$	$1\ 58^{329}$

The moments of compounds of MX_3 type vary to some extent in different solvents The results indicate a series of inequalities, the moments of the following molecules descending in the order $SbCl_3$, $AsCl_3$, PCl_3, PBr_3, PI_3. Here $SbCl_3$ may be supposed to be of pyramidal form with the most acute apical angle in the series, whilst PI_3 is the flattest molecule. It is evident that increasing radius of M and of the halogen X act in opposite directions in these cases.[287] The change in moment from PCl_3 to PI_3 is also opposite to that from NH_3 to AsH_3.[330]

Malone and Ferguson[329] have prepared an electronegativity scale, based on the order of the X–H link moments : increasing electronegativity follows the order As, P, I, S, Br, Cl, N, O, F (see this Vol : 39Aa). Appreciable moment is predicted for all trihalides of the fifth group, except PI_3 and NCl_3, where the atoms concerned do not differ greatly in electronegativity.

Solid AsF_3 has the moment 5·7.[329] Addition compounds of trihalides with organic compounds have been studied.[331] The zero moment of $AlBr_3$ in CS_2 may be attributed to association to form Al_2Br_6 molecules (The result was obtained by the optical refraction method, and not by extrapolation to infinite dilution)

Symmetrical tetrahedral models have been proposed for $SiCl_4$,[336] $TiCl_4$,[336] SnI_4[328] and $GeCl_4$.[328] In the case of $SnCl_4$, moments of 0·8[336] and 0[328,334] are recorded. The symmetrical structures are confirmed by the X-ray evidence (this Vol. : 8), whilst the moment of $SnCl_4$ may perhaps be explained by a somewhat deformed tetrahedral structure. Various organic addition compounds of $TiCl_4$ and $SnCl_4$ have been examined,[332] also organic ethyls of $SnCl_4$.[334] The moment rises considerably on replacing two Cl's by ethyl groups, but falls off again to $Sn(C_2H_5)_4$, where symmetry is again restored. Bergmann and Engel's results on $TiCl_4$ and $SnCl_4$ have been questioned by Ulich and collaborators.[337]

Simons and Jessop[333] have found zero or very small moments for PCl_5 and $SbCl_5$ in CCl_4. Bergmann and Engel,[336] however, found a moment for $SbCl_5$ in CCl_4 of 1·14, a widely different result. It is suggested that in compounds of this type the presence of moment may be attributed to one Cl atom being differently attached from the other four to the central atom. The model suggested is like that proposed for $Fe(CO)_5$, with four attached groups at the corners of a square basal plane of a pyramid, the other group occupying the apex. The central atom will lie somewhere on the middle line of the pyramid perpendicular to the base and passing through the apex. In view of the conflicting experimental evidence, however, no great weight need be attached to this suggestion, until the question of presence or absence of moment in compounds of this type is cleared up.

Bergmann and Engel[336] have suggested a simple relation between the nearest distances M–X in compounds of the above types MX, MX_2, MX_3, MX_4 and MX_5, as follows :—

$$r_{A \rightarrow X} = \sqrt[3]{\frac{3P_E}{4\pi N}} = \sqrt[3]{0{\cdot}394 P_E} \quad \dots\dots\dots\dots \quad (19)$$

This formula was applied to internuclear distances of the chlorides, in order to ascertain the separations B–Cl, P–Cl, As–Cl, Sb–Cl and Sn–Cl. Taking the radius of the Cl atom as 1·07, it was possible to deduce the atomic radii of the non-halide atoms, with good general agreement with independent evidence. On the other hand, the relation gave too low values for the internuclear distances of the hydrogen halides HX. The assumption virtually is $r_e^3 = \alpha$, the polarizability. Clark[215] has shown that strict equality does not hold, but that proportionality between a and r_e^3 is observed for the halides, according to the relation

$$a = 1{\cdot}242 r_e^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

A similar relationship has been suggested by Goss,[340] as lows :—

$$r_e = \sqrt{\frac{4P_E}{3\pi N f}} = \sqrt[3]{\frac{16a}{9f}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (21)$$

The "polarizability factors" f of a number of simple di-atoms have been calculated, and shown to stand in linear relationship with the group number n in a given period. Hückel[338] has criticized Bergmann and Engel's work on the basis of equation (19) on the ground that it gives only upper limiting values of internuclear distances, and that, especially when considerable dipole moment is present, the errors may be large, as great as 10% ($SbCl_5$) The authors have replied to this objection.[339] By combining (19) and (21), we get an upper limit for f = 16/9 1·78.

Bergmann and Engel's research has also been subjected to some criticism on the ground of experimental detail.[337] In spite of this, the work seems to constitute a notable advance in the application of stereochemistry to the Clausius-Mosotti formula.

(L) **Silver and Lithium Perchlorates.** The solubility of $AgClO_4$ in C_6H_6 has been examined by Hill,[296] who found indication of complex formation $AgClO_4C_6H_6$. Williams and Allgeier[230] assigned the large moment 4·7 to the molecule in dilute solution in benzene The still larger moment of 7·84 has been assigned to $LiClO_4$ in dioxane.[329]

(M) **Cases of Zero Moment.** In addition to cases mentioned in preceding sections, the following have zero, or very small, moment : Na, K, P and S and the gases He, Ne, A, Kr, Xe, H_2, O_2, N_2 and SF_6[43] The symmetry of the diatomic gases H_2, O_2 and N_2 is confirmed by the absence of infra-red absorption bands from their spectra.

Attention may be called to the fact, previously noted, that the polarization of CO_2 and NH_3 increases slowly with density in defiance of the requirements of the Clausius-Mosotti law, whilst the polarization of CH_4, N_2 and H_2 is independent of density.[342] No satisfactory explanation of these results appears to have been found.

It may be argued that some of the results described in foregoing paragraphs may be inapplicable to the free molecules on account of possible interaction with the solvents employed. Definite evidence of such interaction exists in some cases, and seems to be indicated wherever the moment of a given substance varies in different solvents. Such interference can perhaps only be considered to be entirely eliminated in cases where the molar polarization of the solute P_2f_2 gives a linear relation with concentration, that is, where the contribution P_2 made by the solute is constant. Fortunately, in a considerable number of cases, this condition is fulfilled: where it is not, it must appear that deductions which neglect the possibility of interaction must still be accepted with some reserve.

43. Dipoles and the Kerr Effect

(A) **General and Theoretical Results.** It was discovered many years ago by Kerr that *carbon bisulphide* became doubly refractive for a light ray passing perpendicular to the direction of an applied electrostatic field, the difference in refractive index for vibrations in two directions at right angles being proportional to the square of the field intensity for a given wavelength.[343] Cotton and Mouton[344] observed the similar effect for an applied magnetic field. The further study of these phenomena in more recent times has thrown much light on the problem of molecular structure in connection with the theory of polar molecules.

Figure LXXXVII depicts two parallel plates between which a large difference of potential V may be maintained in the medium placed between them. Let a plane polarized light ray pass in the direction OY parallel to the plates, the vibrations being at right angles to OY. If the polarizing and analysing nicols are set so that no light escapes at Y, it is found that light begins to pass the second nicol when the field is applied along OZ, at right angles to OY. Then according to the Kerr

Effect, the indices of refraction for vibration components of the light parallel to OZ (r_z) and to OX, at right angles to OZ (r_x), will be different, the difference being proportional to square of field strength E^2 for given wave-length λ. The

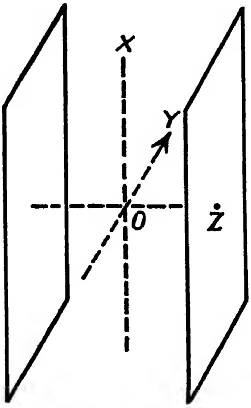


FIGURE LXXXVII.—THE KERR EFFECT.

general formula for the Kerr constant B for a vapour sufficiently rarefied to obey Boyle's Law is then

$$B = \frac{r_z - r_x}{\lambda E^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (22)$$

The phase difference $[\Delta D]$ is given by the relations

$$[\Delta D] = \frac{2\pi l(r_z - r_x)}{\lambda} = 2\pi BlE^2 = 2\pi[\Delta\lambda] = 2\pi Bl\frac{V^2}{a^2} \quad .. \quad (23)$$

where l is the length of the light path, and a is the distance between the plates. These equations embody Kerr's Law.

The Kerr Effect has found interpretation in terms of the optical anisotropy of molecules, according to which their induced polarizabilities may be different in different directions. Normally, a group of anisotropic molecules behave as if isotropic, because the molecular axes are distributed at random in different directions, so that the net effect in any one direction is the same. The Kerr Effect is of importance in revealing the anisotropy of individual molecules. Havelock[345] related together the Kerr and ordinary dispersion, as follows :—

$$B = \frac{c}{E^2} \frac{(r^2 - 1)^2}{r\lambda} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (24)$$

where r is the ordinary refractive index, and c is a constant independent of λ, a relation known as Havelock's Law. Silberstein[346] examined departures from additivity of molecular refraction, and concluded that contributions made by isotropic atoms cannot give correctly the resultants of anisotropic molecules by simple addition. The transverse and axial refractivities were calculated in simple cases, and it was found that neither possess strictly additive character.

In respect of its optical distortion, a molecule may be represented by a polarization ellipsoid, having three perpendicular axes, along which the polarizabilities are respectively b_1, b_2, b_3 so that the mean polarizability a is given by—

$$a = \frac{b_1 + b_2 + b_3}{3} = \frac{r^2 - 1}{r^2 + 2} \cdot \frac{3}{4\pi N} \quad \ldots\ldots\ldots (25)$$

where N is the number of molecules per c.c. of medium. In an electric field, the molecules will tend to set themselves so that the direction of highest polarizability will be parallel to the field direction, except when $r_x > r_s$ and B becomes negative.

Gans[347] found that the optical anisotropy of a molecule might be measured by a quantity δ, related to the depolarization factor Δ (ratio of intensity of light scattered parallel and at right angles to the direction of the incident beam), as follows—

$$\delta^2 = \frac{5\Delta}{6-7\Delta} = \frac{(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2}{2(b_1 + b_2 + b_3)} \quad \ldots\ldots (26)$$

For completely symmetrical molecules, $b_1 = b_2 = b_3$, so that $\Delta = \delta = 0$ (see this Vol.: 45). The Δ's are not, however, always accurately known from experiment.

Langevin[348] gave an account of the Kerr Effect on the basis of the optical and electrostatic anisotropy of molecules, the orientative action of the applied field being due to the couple exerted by it on the induced dipoles of the molecules of the medium. Born[349] extended the theory to take account of the effect of the field on permanent electric dipoles, if any, which may be present. A convenient summary of the argument has been given by Beams,[350] so that results only need be given here. Other works which may be consulted are due to Meyer and Otterbein,[351] Wolf, Briegleb and Stuart,[352] and Stuart and Volkmann.[353,354]

The result of the Langevin-Born theory may be expressed as follows, in terms of new Kerr constants K, K_1, K_2 :—

$$K = \frac{B\lambda}{r} = \frac{r_{\parallel} - r_{\perp}}{rE^2} = \frac{\pi N}{3r^2}\left[\frac{(r^2+2)(\epsilon+2)}{3}\right]^2(\theta_1+\theta_2) = K_1+K_2 \quad \ldots (27)$$

where

$$\theta_1 = \frac{1}{45kT}[(a_1-a_2)(b_1-b_2)+(a_2-a_3)(b_2-b_3)+(a_3-a_1)(b_3-b_1)] \quad \ldots\ldots\ldots\ldots\ldots\ldots (28)$$

and

$$\theta_2 = \frac{1}{45k^2T^2}[(\mu_1^2-\mu_2^2)(b_1-b_2)+(\mu_2^2-\mu_3^2)(b_2-b_3)+(\mu_3^2-\mu_1^2)(b_3-b_1)] \quad \ldots\ldots\ldots (29)$$

The Kerr constant K may thus be split up into two parts, K_1 $(=3\pi N\theta_1)$ and K_2 $(=3\pi N\theta_2)$, of which K_1 refers to the induced polarizabilities and K_2 to the permanent electric dipoles. The values of a_1, a_2, a_3 correspond to the electric polarizabilities along the three axes under the applied electric field. The moments μ_1, μ_2, μ_3 are the components of μ along the same optical axes k is Boltzmann's constant, and T the absolute temperature. Molecules without permanent moment have $K = K_1$, $K_2 = \theta_2 = 0$.

The three relations (25), (26) and (27) enable estimates of b_1, b_2 and b_3 to be made. In general, the equations take somewhat simpler forms in the case of gases (see Section B below). The direction of the permanent dipole may also lie along one or other of the axes of the optical ellipsoid, enabling certain simple conclusions to be drawn. Thus if $b_2 = b_3$, for $\mu = \mu_1$, $\mu_2 = \mu_3 = 0$, $\theta_2 = 2\mu^2(b_1 - b_2)$, whilst for $\mu = \mu_2$ or μ_3, with the other two components of moment respectively zero,

$\theta_2 = -2\mu^2(b_1 - b_2)$. Hence θ_2, and therefore K_2, is positive when the dipole lies along the axis of greater polarizability, and negative when the dipole is at right angles to the axis. In the latter case, if $K_2 > K_1$, $K = K_1 + K_2$ will be negative also. The following results should hold:—

(a) K, and therefore B, can be either positive or negative;

(b) K_1 can only be positive;

(c) K_2 can be positive or negative: when positive, the dipole lies along the axis of greatest polarizability, and when negative, the dipole is inclined to this axis;

(d) a diatomic molecule has the direction of greatest polarizability along its internuclear line;

(e) a plane molecule has the greatest polarizability in the plane, and the least at right angles to the plane.

It is noteworthy that molecules having dipole moments often have negative Kerr constants, especially when the moments are relatively large, and that no molecule known to lack permanent moment has ever been found to have a negative constant This provides a striking confirmation of the theoretical predictions

(B) **Results on Gases.** We may first simplify the relations given in the preceding sub-section to the case of gases, where (a) the refractive index r does not differ appreciably from unity, (b) there is an axis of symmetry, so that $b_2 = b_3$.

Equation (25) then gives

$$a = \frac{b_1+2b_2}{3} = \frac{r^2-1}{r^2+2} \cdot \frac{3}{4\pi N} = \frac{(r+1)(r-1)}{r^2+2} \cdot \frac{3}{4\pi N} \sim \frac{2(r-1)}{3} \frac{3}{4\pi N},$$

so that

$$a = \frac{r-1}{2\pi N} = \frac{b_1+2b_2}{3} \quad \ldots\ldots \quad \ldots\ldots \quad (30)$$

The Gans relation (26) takes the form

$$\delta^2 = \frac{5\Delta}{6-7\Delta} = \frac{(b_1-b_2)^2}{(b_1+2b_2)^2},$$

or, putting $(b_1+2b_2)^2 = 9a^2$,

$$(b_1 - b_2)^2 = \frac{45\Delta}{6-7\Delta} a^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (31)$$

Further, equation (27) reduces to

$$K \backsim B\lambda \backsim \frac{\pi N}{3}\left(\frac{3 \cdot 3}{3}\right)^2 (\theta_1+\theta_2),$$

so that

$$K = 3\pi N(\theta_1+\theta_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (32)$$

Gans[347] also introduced the approximations

$$\frac{a_1}{b_1} = \frac{a_2}{b_2} = \frac{a_3}{b_3} = \frac{r^2_\infty - 1}{r^2-1} = \frac{r_\infty - 1}{r-1},$$

so that (28) becomes, on substitution,

$$\theta_1 = \frac{1}{2kT} \cdot \frac{(r-1)(r_\infty - 1)}{\pi^2 N^2} \cdot \frac{\Delta}{6-7\Delta} \quad \ldots\ldots\ldots \quad (28a)$$

giving, by $K_1 = 3\pi N\theta_1$, inserting the values of the constants, at N.T.P.,

$$K_1 = 4 \cdot 72 \times 10^{-7}(r-1)(r_\infty - 1) \cdot \frac{\Delta}{6-7\Delta} \quad \ldots\ldots \quad (33)$$

Finally, if $\mu = \mu_1$, and $\mu_2 = \mu_3 = 0$, from (29),

$$\theta_2 = \frac{\mu^2}{45k^2T^2}(2b_1 - b_2 - b_3) \quad \ldots\ldots\ldots\ldots\ldots \quad (34)$$

which undergoes further simplification when $b_2 = b_3$.

A few results on non-polar molecules are first considered. *Chlorine* Cl_2[352,353] has $r_D = 1 \cdot 000782$, $\alpha = 4 \cdot 61 \times 10^{-24}$, $\Delta = 0 \cdot 043$, $\mu = 0$, $K_2 = 0$, whence, by equations (30) and (31), $b_1 = 6 \cdot 60 \times 10^{-24}$, $b_2 = b_3 = 3 \cdot 62 \times 10^{-24}$. Further, $r_\infty = 1 \cdot 00076$, so that, by (33), $K_1 = +2 \cdot 1 \times 10^{-15}$, in good agreement with the experimental figure $2 \cdot 3 \times 10^{-15}$ (Na–D line, 760 mm., 24°C.) Here the b_1 is the internuclear axis of symmetry, and the direction of greatest polarizability, in accordance with the positive sign of the Kerr constant. Other linear, non-polar molecules treated in similar fashion have yielded the following results: *acetylene* C_2H_2, $b_1 = 5 \cdot 12$, $b_2 = b_3 = 2 \cdot 43$; *carbon dioxide* CO_2, $b_1 = 4 \cdot 10$, $b_2 = b_3 = 1 \cdot 93$; *carbon bisul-*

e CS_2, $b_1 = 15{\cdot}14$, $b_2 = b_3 = 5{\cdot}54$; *nitrous oxide* N_2O, $= 5{\cdot}32$, $b_2 = b_3 = 1{\cdot}83$ $(\times 10^{-25})$. In all these cases, the b_1 is an axis of symmetry. There is some doubt, as already pointed out elsewhere, whether the dipole moment of nitrous oxide is zero. The Kerr Effect gives K (expt) $= 3{\cdot}08$, K_1 (calc. by (33)) $= 2{\cdot}68$, so that $K_2 = K - K_1 = 0{\cdot}4 \times 10^{-15}$, which gives an upper limit for μ of $0{\cdot}14$. Hence the linear, but unsymmetrical, model $N \equiv N = O$ is suggested, in agreement with independent evidence. Sometimes relatively large K's occur even for non-polar molecules, as in the case of CS_2 $(K = 21{\cdot}0 \times 10^{-15})$.

As an example of a plane molecule without moment, we may cite *benzene* C_6H_6, for which $K = 5{\cdot}8 \times 10^{-15}$ at 760 mm. and 105°C., $\Delta = 0{\cdot}042$, $r_D = 1{\cdot}001821$, whence $b_1 = 6{\cdot}76$, $b_2 = b_3 = 12{\cdot}7 \times 10^{-24}$. Here b_1 measures the polarizability perpendicular to the ring plane, whilst b_2 and b_3 are in the plane.[353] *Stannic chloride* $SnCl_4$ provides an example of a non-polar, non-planar molecule.[353] It is found that $K_2 = 0 \pm 0{\cdot}5 \times 10^{-15}$ and the anisotropy appears too small to support the pyramidal model of Bergmann and Engel, with $\mu = 0{\cdot}8$.[336] Taking the Sn–Cl distance as 2·36, and Cl–Cl as at least 3·0, an upper limit for the pyramidal height is found to be 0·95. For such a flat pyramid, the axis of greatest polarizability would lie in the plane of the four Cl atoms, and the anisotropy would be considerable. This argument therefore indicates tetrahedral structure for $SnCl_4$.

Ramanathan[372] studied the scattering of light by molecules of *hydrogen*, *nitrogen* and *oxygen*. Assuming spherical symmetry, molecular radii were obtained in close agreement with the kinetic theory " free path " values. It was also found that the carbon atoms in *benzene* were arranged in a puckered formation. It would appear unlikely, however, that the spherical form of the first three molecules studied can correspond to reality, since they are of the dumb-bell diatomic type, whilst the conclusion about the benzene ring does not find confirmation in the X-ray evidence (see this Vol.: 14Aa)

An appreciable difference between K(expt.) and K_1(calc.), or a negative value of K, may be taken to indicate the presence of polar molecules. *Hydrogen chloride* HCl[352,353,354] has K(expt.) $= 5{\cdot}75$ (Na–D line, 760 mm., 18°C), $\mu = 1{\cdot}034$,[220] $r_D = 1{\cdot}000447$, $r_\infty = 1{\cdot}000435$. Taking $\Delta = 0{\cdot}01$, equation (33) gives $K_1 = 0{\cdot}15$, so that $K_2 = K - K_1 = 5{\cdot}60 \times 10^{-15}$. The positive sign of K_2 shows that the axis of greatest optical polarizability coincides with the internuclear line. Stuart and Volkmann[353] give $b_1 = 3{\cdot}13$, $b_2 = b_3 = 2{\cdot}39 \times 10^{-24}$, $\mu = \mu_1$, $\mu_2 = \mu_3 = 0$. Raman and Krishnan[373] reversed the method of calculation, using Kerr constant data to deduce $\mu = 1{\cdot}04$, in good agreement with experiment. Some interesting conclusions also follow by comparing equations (20) and (30), from which it appears that b_1, b_2 are proportional to the cube of internuclear distance for the four halides HF, HCl, HBr and HI. If this is accepted, it follows that the four molecules have equal anisotropies, the constants being $\delta = 0{\cdot}1004$, $\Delta = 0{\cdot}0119$. It is also found that the polarizabilities along the long axis are equal to those of the corresponding negatively charged halogen ions. Clark[355] has thus estimated the Kerr constants of the four gases

Planar molecules having dipole moment are exemplified by *hydrogen sulphide* H_2S,[352] and *sulphur dioxide* SO_2.[354] In each case, b_1, b_2 and b_3 are unequal, the direction of smallest polarizability b_2 is at right angles to the molecular plane, and $\mu = \mu_3$, $\mu_1 = \mu_2 = 0$. For H_2S, $b_1 = 4{\cdot}21$, $b_2 = 3{\cdot}21$, $b_3 = 3{\cdot}93 \times 10^{-24}$ with a small positive Kerr constant, suggesting that the molecule sets itself in an electric field with a direction of greater optical polarizability b_3 along the field direction. SO_2 has $b_1 = 5{\cdot}49$, $b_2 = 2{\cdot}72$, $b_3 = 3{\cdot}49 \times 10^{-24}$, with a negative Kerr constant, so that the dipole direction b_3 is at right angles to the direction of greatest optical polarizability b_1, and the molecule sets itself with a direction of smaller polarizability b_3 in line with an applied electric field. More accurately, perhaps, the difference in the two cases is shown by the relatively large $b_1 - b_2$ in the case of SO_2 as compared with H_2S.

Non-planar, polar molecules are represented by *ammonia*, NH_3,[354] having a pyramidal molecule. The Kerr constant is positive, and the moment lies along the central axis of the pyramid, which is also the direction of greatest optical polarizability. Assuming rotation symmetry about the central axis, the data give $b_1 = b_2 = 21{\cdot}8$, $b_3 = 24{\cdot}2 \times 10^{-25}$.

A large number of other cases have been studied, amongst which may be mentioned *methyl* and *ethyl chlorides, methyl bromide,* n-*propyl chloride, ethyl ether* and *acetone.* The summary of results given by Stuart and Volkmann[353] may be consulted for further information.

The temperature and pressure variation of the Kerr constant has been found to be in agreement with theoretical prediction in the case of gases, including *carbon dioxide.*[356,357,363] The effect of changing wave-length (4,000 to 7,500 Å.U.) has also been studied in this gas, the results being found to be in better agreement with the Langevin-Born theory than with that of Havelock (see equations (24) and (27) above)[358]

(C) **Results on Liquids.** Liquids are generally easier to experiment upon than gases, but the interpretation of the results is much more difficult. This may be due in part on the experimental side to the effect of the presence of impurities, and on the theoretical to the difficulty of allowing for the complex interactions of neighbouring molecules Hehlgans[364] has shown that the deviations in the Kerr constant of *nitrobenzene* may be attributed to impurities, and that for the highly-purified substance Kerr's Law holds.

When molecules of similar structure are compared, it is found that the Kerr constants increase regularly with increase in the values of $P_A + P_O$, the sum of the atomic and orientation contributions to the total polarization of liquids Thus Ebert,[213] using measurements of Leiser, showed a progressive increase of the two numbers from *para-* to *meta-*, and from *meta-* to *ortho-xylol*, also in the two series *benzene, ethylbenzene, toluene; mesitylene, toluene, meta-xylol,* associated with increasing asymmetry of the molecule. Examples may also be found in the aliphatic series of compounds : *carbon tetrachloride* and *tetranitromethane* have very small Kerr constants, unsymmetrical derivatives of methane as *methyl chloride, nitromethane* and *acetic acid* have much higher values, whilst those of *methylene chloride* and *chloroform* are increasingly negative

The attempts to obtain more accurate relations for liquids will be considered quite briefly in view of the still tentative nature of many of the results. Considering non-polar molecules, the relation between the optical constants of a liquid and the depolarization factor Δ are uncertain, but if we may follow Raman and Krishnan,[359] we have a relation of the type (27), with $K_2 = 0$, and instead of (28) and (33)

$$\theta_1 = \frac{9\beta(\epsilon-1)(r^2-1)}{8\pi^2 N} \cdot \frac{\Delta}{6-7\Delta} \quad \ldots\ldots\ldots\ldots \quad (35)$$

where β is the isothermal compressibility of the liquid, and

$$B = \frac{\beta(r^2-1)(r^2+2)(\epsilon-1)(\epsilon+2)}{24\pi r\lambda} \cdot \frac{\Delta}{6-7\Delta} \quad \ldots\ldots \quad (36)$$

This equation was used by Raman and Krishnan[359] to compute B for non-polar liquids, and although the theoretical numbers proved to be of the same general order as the experimental, numerous deviations were found to exist.

In the case of a polar liquid, the value of θ_2 is no longer zero, and may be difficult to estimate, since the ellipsoid of the gas phase may be distorted. The most satisfactory theory proposed up to the present appears to be that of Raman and Krishnan,[360] according to which

$$B = \frac{r^2-1}{4r\lambda} \cdot \frac{3}{a}(\theta_1'+\theta_2') \quad \ldots\ldots\ldots\ldots\ldots \quad (37)$$

where θ_1', θ_2' have the same forms as for gases (28), (29), but the a's and b's have different meanings.[350] Using data obtained by experiments on the scattering of X-rays by liquids (see this Vol. · 16), it is sometimes possible to evaluate B. It is claimed that rather better agreement is obtained than by the use of the Langevin-Born theory. The significance of this modification appears to be that a molecule, itself anisotropic, is assumed to be surrounded by an anisotropic field of surrounding molecules, whereas in the Langevin-Born theory the surroundings are assumed to be isotropic.

An interesting experiment was performed by McFarlan,[362] who replaced the crystal of a Bragg spectrometer by a liquid placed under a potential difference. The effect in *nitrobenzene* indicated that not only does molecular orientation occur around polar centres, but also an irregularity in the spatial distribution of the scattering centres is set up in consequence of the application of an external field.

In this connection, it may be noted that Raman and Krishnan[361] have suggested a modified Clausius-Mosotti relationship for liquids

$$\frac{\epsilon-1}{\epsilon+2} = N\left(\frac{4\pi\alpha}{3} + \frac{\epsilon-1}{\epsilon+2}\psi\right) + \frac{N}{3kT}\left(\frac{4\pi\mu^2}{3} + \frac{\epsilon-1}{\epsilon+2}\theta\right) \ldots \quad (38)$$

where ψ and θ involve the influence of the anisotropy of the medium on $(P_E + P_A)$ and P_0 respectively. Further details are given in the original paper. de Mallemann[392] has also modified the Clausius-Mosotti formula.

Wolf, Briegleb and Stuart[352] examined the data for several liquids, and found that $9K/(\epsilon+2)^2$ increased in the same order as the μ's, in accordance with anticipation from a formula of the type (27). Negative Kerr constants were found for compounds containing NH_2, OH, OCH_3 and OC_2H_5 groups in aromatic compounds. These were explained in terms of angles between the valency directions from the N or O atoms, with consequent inclination of the permanent moment to the plane of the benzene ring. Raman and Krishnan had found earlier that the alcohols had negative constants, the permanent moment lying between 55° and 90° with the direction of greatest polarizability.

In studying the case of liquid mixtures, Briegleb[365] introduced a molecular Kerr constant M_K given by

$$M_K = K\left(\frac{r}{r^2+2}\right)^2\left(\frac{1}{\epsilon+2}\right)^2\frac{M}{d} \quad \ldots\ldots\ldots\ldots \quad (39)$$

and assumed that an additive law of the type

$$M_{K_{12}} = M_{K_1}c_1 + M_{K_2}c_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (40)$$

should hold in cases where interaction between the liquids was absent. Departures from additivity, and variation of the molecular Kerr constant of the mixture with concentration were attributed to mutual influence between the molecules in the case of non-polar liquids, and to association in the case of polar molecules. The variation of anisotropy on passing from gas to liquid showed that the dipole-free molecules C_6H_6, CS_2 and C_7H_{14} are similarly built, with the axis of greatest polarizability in the plane of the ring (C_6H_6) or in the long direction of the molecule (CS_2, C_7H_{14}). Molar Kerr constants in heptane solution extrapolated to infinite dilution were smaller than for the corresponding vapours : thus in the same units, *acetone* gas and solution gave 55·8 and 36·2 respectively. This was attributed to formation of complexes between the solute and the solvent. Amongst other liquids studied in heptane solution were *ethyl ether*, *chloroform*, *toluene* and meta-*xylol*.

In a further communication, Briegleb[366] divided liquid molecules into four types, as follows · (1) dipole-free molecules, which can orientate themselves mutually by the axis and plane of greatest polarizability; (2) molecules with polar groups, which may unite by virtue of their direction of greatest partial moment; (3) molecules which induce moment in other molecules, and so combine ; (4) molecules united by " valency " forces. The dipole-free molecules may be subdivided into (a) those with no polar group present, yet which can exert forces on each other, as *carbon bisulphide*, *benzene*, *naphthalene*, *diphenyl* and *phenanthrene* ; (b) those with polar groups, but without resultant moment, so that θ_1 decreases with increasing concentration by association of the type $\leftarrow \underset{\longleftrightarrow}{\rightarrow} \longleftrightarrow$, as with p-*xylol*, p-*dichlorobenzene*. In the case of dipole molecules, θ_2 decreases by increasing association with increasing concentration, but θ_1 may increase, when association is of the type $\longrightarrow \longrightarrow$, as with *toluene* and *chlorobenzene*, or decrease, when association takes the form $\rightleftharpoons$, as with *acetone*, *chloroform*, and *ethyl ether*. The experimental results were in accord with this theory.

Stuart and Volkmann[367] have contributed to the subject of the molar Kerr constants of liquid mixtures. The M_{K_2} of *nitrobenzene* at infinite dilution (5460 Å U., 20°C.) was found to be 101 in *benzene*, 150 in *heptane*, and 111 × 10^{-12} in *carbon* *tetrachloride.* There was also a variation with temperature in many cases not in accordance with the Langevin-Born theory. These deviations were attributed to association. The authors[368] have also considered the various avenues of approach to the problems raised by the association of liquids. It is found that molecular refraction is largely insensitive to association, and only changes by a small amount on passing from gas to liquid. The orientation polarization, however, is smaller for liquids than for vapours, due to reduction of moment by association. Neither molecular refraction, which measures mean polarizability, nor orientation polarization, which is concerned with the mean moment, takes account of anisotropy, and to this extent may be inadequate experimental guides. The depolarization δ^2 increases with temperature for liquids, finally reaching the value for the vapour: the relatively smaller value for liquids may be attributed to association. The molar Kerr constants are also smaller for liquids than for gases, for which they are independent of pressure. It appears from this that deviations from expectation on the ground of the Langevin-Born equation may be attributed to association, but that no entirely satisfactory theory has yet taken its place. The Raman-Krishnan theory is found to be unsatisfactory, although Narasimhiah[370] has used it in the case of binary liquid mixtures with some success.

An interesting calculation has been made by Otterbein,[369] which may be the forerunner of many further developments Measurements on the Kerr Effect of dilute solutions were made in order to obtain the anisotropies of free molecules, assuming the additivity principle. It was found that the Kerr constants of the *dichlorobenzenes* could be predicted, by tensor addition, from those of *chlorobenzene* and *benzene.* If this can be shown to be part of a wider generalization, Kerr constants may be capable of calculation, as in the case of dipole moments, considered in this Vol.: 39Ac (ii).

An investigation of the influence of field strength by Hootman[371] has shown that Kerr's Law holds to within about 0·1% for pure, non-polar *carbon bisulphide* up to the highest fields the liquid could sustain. In polar liquids, *ethyl ether* and *chloroform,* however, easily measurable deviations with field strength were found.

(D) **Results on Solids.** In considering the Kerr Effect of solids, at least two complicating factors become of importance: (a) time lag, and (b) electrostriction. In his original experiments on glass, Kerr found that the double refraction required several seconds to attain its full value, or to disappear when the field was applied, or removed, respectively. Such an effect is not characteristic of liquids. It is connected with Debye's "relaxion time" (see this Vol.: 31C, end). The formula gives times of the right order of magnitude in the case of viscous liquids. Electrostriction, or the setting-up of strains in the medium by the applied field, introduces double refraction, which may be difficult to disentangle completely from the Kerr Effect Some progress has been made (see [350]).

(E) **The Cotton-Mouton Effect.** The influence of a magnetic field is analogous to that of an electric field, so that we may substitute H (strength of magnetic field) for E in the relations (23), giving Cotton-Mouton's Law. Treatment was given of the effect by Langevin and Born,[350] the equations taking similar forms, with magnetic in place of electrical anisotropies. Ramanadham[374] found the magnetic anisotropy larger amongst the aromatic than the aliphatic compounds, whilst the Cotton-Mouton constant C, which replaces B in (22), (23), is negative for saturated chain compounds and positive for unsaturated compounds containing the carbonyl group or a benzene ring. The lengthening of aliphatic chains without unsaturated bonds tends to increase negative and decrease positive birefringence.[375] The effects in *benzene*, *carbon bisulphide*, and *nitrobenzene* have recently been compared with the Langevin theory.[376] The dissociation of *nitrobenzene* in *carbon tetrachloride* and *hexane* by dilution or heat becomes assisted, with corresponding changes in magnetic double refraction.[377] Piekara[378] has recently examined *acetic acid* and other fatty acids, and *acetic anhydride*, and has discussed the applicability of the Langevin formula, especially with respect to variations in temperature. As in the case of the Kerr Effect, Raman and

Krishnan[391] have provided a modified treatment, based on the assumption of the anisotropy of the field around a molecule due to surrounding molecules in liquids.

Oxygen gas under compression acquires a negative birefringence in a magnetic field proportional to the pressure,[379] similar results having been obtained on *nitrogen.*[380] *Liquid oxygen* was shown in Onnes' laboratory at Leiden to have a strong magnetic double refraction (negative), an observation which has been recently confirmed.[381]

A magneto-optical method for the chemical determination of minute traces of metals, notably calcium, has been described by Allison and Murphy.[385] The minimum light intensity passes the second nicol of a Cotton-Mouton cell when it is set at 0°, and it is claimed that the amount of rotation possible before the minimum disappears depends on the concentration of the compound in the cell solution, so that it is possible to detect traces of substances in parts per 10^{-11} It is reported, however, that the method is unsuccessful, and even capable of yielding absurd results.[386] This is also the general conclusion of Slack,[387] who goes very carefully into the available evidence, and provides a list of 58 papers dealing with the subject.

The magneto-optical effect in the case of *ferric oxide hydrosols*, discovered by Cotton and Mouton, has received much attention, notably by Heller.[388] Marshall[389] has also studied the orientation of sol particles, but in an electric field. Substances obeying Maxwell's relation between dielectric constant and square of refractive index give a positive double refraction, that is, the direction of larger index of refraction turns to lie along the lines of force. In the case of substances which show deviations from the relation, it is usually the other way round, and the birefringence is negative ($r_x > r_z$ in equation (22), so that B is negative). The magnetic double refraction of *iron arc smokes* has also been observed.[393]

(F) **Conclusion.** Attempts have been made by de Kronig[382] to treat the Kerr Effect theoretically from the standpoint of the new quantum mechanics on the basis of the dispersion theory of Kramers and Heisenberg More recently, further analysis has been provided by Neugebauer[383] and Serber,[384] as a result of which it is found that the quantum mechanics, besides leading to the classical Kerr formulæ, gives the anisotropy relation (26), but only as a limiting case.

In addition to the summary of Beams,[350] and others already noted, a paper by Stuart,[390] giving an account of the general application of the Kerr Effect to problems of molecular structure, is worthy of perusal by those interested in this matter. The application to *sulphur dioxide, ethers* and *ketones* is explained in some detail.

Investigations on the Kerr and related phenomena promise to throw much light on the anisotropic behaviour of molecules in optical, electric and magnetic fields. Unfortunately, the data on the experimental side are still meagre, and there seems to be a wide research field which will amply repay further study. Beams[350] says · " In the writer's opinion, there is an urgent need for more good experimental data on the Kerr Effect in both polar and non-polar gases and vapours, including its variation with the wave-length of the light, temperature and density of the gas." After emphasizing the necessity of working over the visible region into the ultra-violet, and examining temperature ranges near the point of liquefaction, he adds : " With these data at hand, our hypothesis concerning the electrical and optical anisotropy of individual molecules can be rigidly tested : also an insight into how they interact with each other in forming a liquid will be obtained."

Summarizing, in the case of non-polar molecules, anisotropy (lack of equivalence of properties in different directions), leads to an orientative couple exerted on them, originally in random distribution, and introduces the effect of double refraction. When polar molecules are considered, the orientative couple may be attributed in part to the presence of permanent dipoles, the contribution K_2 made to the Kerr constant K $(=K_1+K_2)$ varying in different cases, and throwing light, by its positive or negative sign, on the lie of the electric dipole with respect to the axes of the polarization ellipsoid. The Kerr constant tends to increase with increasing asymmetry, and affords evidence of the polarity of molecules in good general agreement with conclusions reached on independent grounds.

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CHAPTER XIV

MOLECULAR FIELDS

44. Historical Introduction

THE present chapter contains a brief review of methods which have been found useful in considering the problem of the various force-fields operating between molecules. A few introductory remarks on the important issues raised by treatment by the new quantum mechanics are made in Section 47 below, no serious attempt being made to deal with the subject in this place (see Vol. 3: Chapters XII, XIII, XIV, XV)

The deviations of gases from the requirements of Boyle's Law at high pressures and the phenomena associated with their condensation into liquids require the postulation of an attractive or cohesive field between molecules even where permanent dipole moment is absent. Historically, there have been four leading methods of approach to the problem of molecular fields, which may be referred to as (i) the "classical" treatment, (ii) the van de Waals method, (iii) the method of "intrinsic repulsive" fields, and (iv) the treatment of the new quantum theory. The classical treatment was statistical, and was concerned with the probable distribution of molecules van der Waals assumed the molecules of a gas to be hard impenetrable spheres of finite and invariable molecular diameter, and found a shortening of the mean free path leading to the expression $P = RT/(V - b)$ for the pressure P, where b represents the fourfold molecular volume. To the right side of this equation the quantity $-a/V^2$ was added, where a is the "van der Waals' constant" for the gas. The latter correction was made as an outcome of certain general considerations drawn from

Laplace's theory of capillarity. This led to the familiar relation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

which was found accurately to reproduce the isotherms of a gas-liquid system. The equation is not, however, strictly applicable to liquids. The third method of treatment involves the assumption that in collision a pair of molecules come within the range of each other's repulsive fields, which operate over a very thin shell surrounding the boundaries of the molecule. This means of attack upon the problem has been used by several authors, notably by Lennard-Jones (see Vol. 1: 19A, 33A). The assumption involved may be expressed by means of the equation for the force F between two molecules :—

$$F = -\frac{a}{d^m} + \frac{b}{d^n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where a, b are constants for a given gas, m, n are the exponents of the attractive and repulsive forces respectively ($n > m$), and d is the distance between the centres of the molecules. The van der Waals model may then be viewed as one in which n is very large. It has been found that $n = 15$ accounts for the physical properties of certain gases.

45. Attractive and Repulsive Fields

From the experimental result that the refractive indices and dielectric constants of gases are greater than the corresponding quantities for a vacuum, it becomes necessary to suppose that the electrons of which atoms are composed are movable under the influence of light or an applied electric field, yielding induced polarization. This will happen in a similar way when one molecule enters the field of another.

A molecule without permanent moment sufficiently far removed from other molecules and all polarizing agencies may be supposed to be so constituted that the centres of gravity of positive and negative charges accurately coincide. Let another molecule of the same kind approach this isolated molecule in such a way that their fields begin to exert mutually polarizing effects. The potential energy of a dipole induced by a field F does not vary as F, but as F^2 (see Appendix 2(b) at end of this chapter), so that a computation of the "average squared" field $\bar{F}^2$ will lead to an expression for the potential energy between any two molecules in the case where a large number of molecules are present, as in an actual gas. Moreover, although the net effect of all molecular fields is zero, it is found that $\bar{F}^2$ does not vanish as $\bar{F}$ does owing to chance orientation. Thus the interaction of two dipoles gives rise to an attractive term, whatever their orientation. This leads to the observed force of attraction between gaseous molecules.

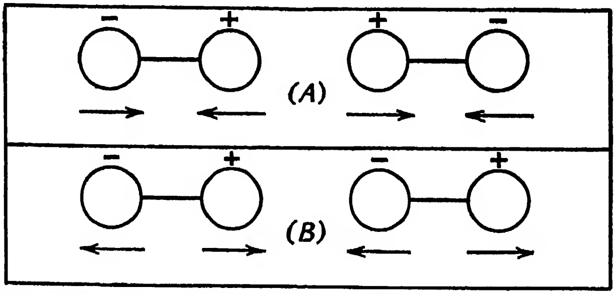

FIGURE LXXXVIII.—INTERACTION OF TWO DIPOLES ON APPROACH. A represents the case where the two fields are oppositely directed, B where they are in the same direction

This suggestion regarding the origin of the van der Waals cohesive force was made by Debye,[1] with the following illustration. Let A in Figure LXXXVIII represent the end-on approach of two dipoles in such a way that the fields of the two are oppositely directed. There is a repulsive force therefore between them which tends to shift the individual charges in the directions of the small arrows. The dipole distances and therefore the dipole moments are reduced, so that the repulsion is decreased, which amounts to the presence of a subsidiary attractive force. In B of Figure LXXXVIII, the dipoles approach in such a way that the force between them is one of attraction, and the fields are in the same direction, causing shiftings of the charges constituting the dipoles in such a way that their dipole moments are increased. Thus the force of attraction is further increased by interaction. It therefore happens that in all cases there is an attractive effect, by interaction between two dipoles tending to decrease repulsion or increase attraction as the case may be. The argument may be extended to the more general case of the approach of dipoles at any angle.

The theory gives an explanation of the cohesion of the inert gases. Helium is the most difficult of the series to liquefy, because its atom is the smallest and therefore the least polarizable. Hydrogen is correspondingly difficult to condense. The behaviour of diatomic homopolar gases has been explained by Keesom[2] as due to the presence of polarizable molecular *quadrupoles*, at any rate for high temperatures and diluted state. The Bohr model of a hydrogen atom assumes an electron to be rotating in orbital motion about a positive charge of equal magnitude to that of the electron. Such a model finds an electrostatic analogy in a rod equally and oppositely charged at opposite ends, representing a dipole. A Bohr model hydrogen molecule assumes two electrons, opposite to each other in the same orbit, revolving midway between the two positive charges. There are then four charges in the molecule, which may be regarded as forming two dipoles so situated as to compensate their electric moments and to constitute a quadrupole. Two such molecules on approach may then be supposed to direct each other in such a way that attractive forces arise as in the cases considered by Debye.

Langmuir's classification of the effects of the force-fields of molecules is noted elsewhere (Vol. 1: 33D).

A molecule whose field is entirely attractive seems artificial, because some repulsive force must balance the attraction. Such a field may be supposed to operate mainly at very short distances, the exponent of the repulsion potential being large. The origin of the repulsive field is not so easily understood as in the case of attraction. In the case of a Bohr hydrogen atom, it is possible to conceive of the electron as equivalent in effect to three hypothetical half-charge negative particles and one half-charge positive particle (Figure LXXXIX).[3] This arrangement is equivalent to a negative electric field (due to $-\frac{1}{2}e$, $-\frac{1}{2}e$) associated with a pulsating field produced by a rotating dipole (due to $-\frac{1}{2}e$, $+\frac{1}{2}e$). The action of such a time-variable field has been shown to result in an average repulsive force being exerted on an outside electron (Debye). Such considerations offer some help in understanding the origin of repulsive molecular fields, but a better explanation arises in the new quantum mechanics (see this chapter · 47)

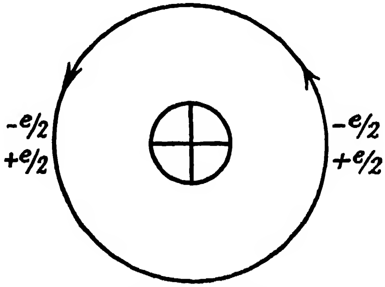

FIGURE LXXXIX—ILLUSTRATION OF THE POSSIBLE ORIGIN OF THE REPULSIVE FIELD OF THE HYDROGEN ATOM.

46. Applications

It is found that, in the case of an inert gas atom outside a crystal of NaCl type (Vol. 1: 33A) considered by Lennard-Jones, the van der Waals' force preponderates over the electrostatic force at considerable distances. Thus it may be assumed that the *process of adsorption* of the inert gas atom at the crystal surface may be explained by the atom being picked up by the van der Waals' force and so brought within the region where the strongly attractive electrostatic field predominates.

The treatment of the molecular field adopted by Lennard-Jones, based on an equation of the type (2), accounts for the *deviation of gases from the ideal laws.* Moreover, the values of n, the repulsive exponent, can be applied to ions similar in structure to the inert gas atoms, valuable information being thereby obtained as to *the lattice energies of ionic crystals.*[4]

The values of the van der Waals' constant a in equation (1) are found to be approximately constant for isomeric organic substances.[5] Where substances of different molecular weight M are compared, it is found that the function aM^2 increases with increasing *molecular asymmetry.* Thus the value of this function for *ethane* (CH_3CH_3) is 9·7, and for *methyl alcohol* (CH_3OH) and *methyl acetate* (CH_3COOCH_3) 19·6 and 82·1 respectively. Further relations in this connection have been traced by van Liempt.[6]

Molecular fields have been studied specially in relation to the *variation of the viscosity of a gas with temperature.* Maxwell found that the viscosity is independent of density, but varies as the square root of the absolute temperature. The latter relation is not fulfilled, and Sutherland[7] proposed an improved formula for viscosity in which $T^{\frac{1}{2}}$ was divided by $1 + (C/T)$, where C is a quantity directly proportional to the work required to separate two molecules of the van der Waals' type from contact to infinity, and therefore closely akin to the constant a in equation (1).[8] It is found, however, that this correction fails to represent the facts for many gases at low temperatures, and does not apply to helium at any temperature. Maxwell realized that the difficulty lay to a large extent in lack of allowance for the effect of molecular fields. The problem has been largely solved by Enskog,[9] Chapman[10] and Lennard-Jones.[11] It is shown by the last-named author that all the known facts can be accounted for, at any rate qualitatively. This work has emphasized the necessity of considering both the attractive and repulsive fields in kinetic problems.

It is necessary to take molecular fields into account also in relation to the *dispersion of light.* Debye's theory of dispersion for the hydrogen molecule is based upon a periodic disturbance of the motions of electrons in Bohr orbits under the influence of a light beam The theory has been tested by Kirn,[12] who has found deviations which become specially marked for shorter wave-lengths A large number of attempts have been made to improve the theory.[13]

According to Rayleigh's theory of scattering, for a beam of unpolarized light, the scattered light is partly polarized, yielding two components, of equal mean intensity. The theory has been subjected to careful investigation by Strutt,[14] and Cabannes.[15] The condition of equal intensity appears to be accurately fulfilled for *argon* and *neon*, but there are wide departures in the case of *helium*.

By a somewhat more complicated procedure than that of Rayleigh, the formula for the depolarization factor Δ is obtained (see equation (26) of Chapter XIII).[16] Molecules whose properties are the same in all directions have $\Delta = 0$, and are isotropic. Anisotropy may therefore be measured in terms of this number. The following shows values of the ratio Δ, some of which, however, may not be very accurate :—

H_2	0·022	A	0·00	N_2	0·037	C_2H_2	0·12	NO	0·026	CO	0·017
He	0·42	Ne	$<$0·01	O_2	0·064	C_6H_6	0·06	N_2O	0·122	CO_2	0·098

It is surprising that *helium* should show so great evidence of lack of electrical symmetry. The deviations of the values for pairs of isosteres *nitrogen, carbon monoxide* and *nitrous oxide, carbon dioxide* are also striking.[3] Molecular asymmetry corresponds to asymmetry of external field.

Returning now to polar crystals, we recall that the work on atomic structure factors (Appendix to Part I, especially references [5,42]) has confirmed the ionic structure postulated by the Braggs. Born and Landé,[17] using an equation of type (2), deduced that the lattice energy of a crystal U should be related to the repulsion exponent n by an expression which for uni-univalent crystals reduces to—

$$U = \frac{329{\cdot}7A}{d}\left(1 - \frac{1}{n}\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

where A is Madelung's constant. The compressibility of a crystal β is then given by

$$\beta = \frac{2{\cdot}829 \times 10^{-13}A}{n - 1} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

Slater[18] measured the compressibilities of eleven *alkali halides,* and so obtained values of n. In his calculations of atomic radii, Pauling[19] derived an expression for the dependence of radius on the valency of an ion, involving n (see Vol. 1 : 19C). These researches, in conjunction with the work of Lennard-Jones, have led to $n = 9$ for many ionic crystals (perhaps the lower value $n = 5$ applies to helium-like ions). This matter is more fully dealt with in another connection, so that it may suffice here to refer the reader to the summary by Sherman[20] for further information.

London[21] found that the van der Waals' potential might be represented by an inverse sixth power term. It has been found, further, that the polarization in an ionic lattice is roughly of the same magnitude as that due to van der Waals' force, involving d^{-6}. The theory was applied to *potassium chloride.*[22]

Born and Mayer[23] have evolved an improved theory, in which the repulsive potential is expressed, not as an inverse power, but as an exponential function of lattice distance, in which the Coulomb, van der Waals and repulsive energies are taken into account. The expression obtained involves two constants for each ion, from which it is possible to calculate lattice distances of *alkali halides* within the probable errors of experimental determination. The formula was applied by Mayer and Helmholtz[24] to the calculation of the lattice energies of alkali halides and the electron affinities of the halogens with conspicuous success The work has been extended to the lattice energies and distances of *silver* and *thallium halides.*[25] It is found that there is some homopolar bonding in AgBr, whilst in AgI the homopolar potential accounts for 10% of the total lattice energy. Similarly, for the *cuprous halides,*[26] and particularly for the iodide, homopolar bonding is present. It has also been possible to account for the superior stability of the cube-centred cubic lattice of *cæsium chloride, bromide* and *iodide*[27] Evjen[28] has carried out a new analysis of Slater's compressibility data, as a result of which it is found that interionic repulsive forces may be calculated either by an inverse power or exponential law.

Pauling[29] has assumed the presence of covalent links in cases where bonding energies are found to be additive : in such cases, the dissociation energy of XY will be the mean of those of X_2 and Y_2. It is found that *hydrogen chloride, bromide* and *iodide* are mainly covalent (homopolar), *sodium* and *potassium chlorides* are ionic, whilst *hydrogen fluoride* and the *alkali hydrides* have intermediate character. Similarly, departures from the rule of additivity for interatomic distances may indicate polar union, as in the case of *potassium chloride,* for which $d = 2{\cdot}65$, whilst additivity gives 2·93 Å.U.[30] In this connection, it may be of interest to note that additivity of internuclear distances has been found to hold very well in the case of gas molecules, as deduced from band spectra, except for metallic molecules such as *lithium* Li_2.[31] The band spectroscopic data gives the distance Li–Li as 2·67, whilst twice the radius of Li, as deduced from crystals, is 3·00. This may perhaps be connected with a kind of linkage in metallic gas molecules, perhaps of van der Waals' type, different from the covalent linkages which give agreement with crystal data and the additivity rule.

The presence of semi-polar bonds, where both electrons for a link are provided by one atom, is generally indicated by high dipole moment, as in the cases of *diphenyl sulphoxide* and *sulphone.*[32] See, further, this Vol. : 27Ab, and [33].

Rice[34] has calculated the attractive potential in metals of the *alkali* and *alkaline earth group,* on the assumption of the presence of positive ions surrounded by electrons, and has deduced heats of sublimation in satisfactory agreement with experiment. Further information concerning linkages in metals will be found in Vol. 1 : 33D.

47. Note on the New Quantum Mechanics

The fundamental conception of the new quantum mechanics arose in the work of de Broglie. It was found that a particle of matter in motion was mathematically equivalent to a group of waves. Certain experiments of Davisson and Germer and of Thomson have suggested that electrons behave like wave motion, for example, in reflection from a nickel surface (see this

Vol.: 49 and Vol. 3: 55F). The development due to Schrödinger was the introduction of a fundamental wave equation, by means of which, without any empirical data, it became possible to calculate molecular and spectroscopic constants with accuracy. The theory embodies the conception that atoms and molecules possess a continuous structure, represented by a variation in density of electric charge at different distances from the nuclear centres, so that contours of equal electron distribution may be drawn. The electron distribution within a given small element of volume dV may be regarded as proportional to the time spent by an electron in that volume, determined by considerations of probability. The idea, due to Bohr, of electrons moving in orbits is abandoned, the quantum emission of radiation by atoms and molecules being regarded as the result of energy distribution changes throughout the whole systems. An isolated atom or ion has a spherically symmetrical electron contour distribution about the nucleus as centre, the charge distribution falling to a small value at a certain distance corresponding to the " radius " of the atom or ion, but extending, at least theoretically, in all directions to infinity. It is possible, by means of the theory, to consider the interaction of two systems, say two hydrogen atoms to form a hydrogen molecule.

The conception that ions with completed sub-groups of electrons are spherically symmetrical has replaced Born's idea that repulsive forces may arise from interaction of electric moments between two particles. According to the newer view, mutual interpenetration of ions introduces repulsion between their nuclei [35] Born's polarization formula $E = e^2a/2d^4$ (see Appendix to Part II: 2(b)) seems to be only an approximation, and to be particularly inaccurate at small distances of approach of two interacting fields. In the case of interaction of a proton with a hydrogen atom, for example, the new quantum mechanics gives smaller energy E values than those deduced by Born's formula Pauling[36] has even expressed the view that better results are obtained by neglecting polarization in molecular structure than by using Born's relation.

Heitler and London[37] attempted to calculate the bonding energy of the hydrogen molecule by the interaction of two atomic wave-functions (Vol. 3: 54F, 55C). James and Coolidge[38] appear to have effected an improvement in the method by introducing a molecular wave-function, in which the idea of separate atomic functions loses its meaning. At the moment, our purpose is to do no more than state that it is possible to calculate molecular constants by the wave-theory of atomic structure with considerable accuracy. For example, Hylleraas [39] treated the lithium hydride polar lattice by the new methods and, without the introduction of any empirical data, calculated the lattice energy of LiH as 219 Cal., as against 218 Cal., obtained by the use of a Born cycle.

It is important to observe that the results are obtained from a consistent mathematical theory, starting from first principles, independent of assumptions made in earlier attempts. The analysis is unfortunately very difficult, and has so far only been applied in relatively simple cases. Its initial achievements, however, justify the belief that the method of argument involves the most valuable means of approach to the problem of molecular fields so far discovered. Although from some points of view it may be desirable to retain orbital atomic models, the new theory has already provided a deeper insight into problems of simple atomic and molecular structures and of interacting fields than has been reached at any time in the past.

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APPENDIX TO PART II

POTENTIAL ENERGIES OF DIPOLE SYSTEMS

(1) **General** (Figure XC).

According to the Coulomb Law (equation (1) of Chapter X), the force f between two particles carrying equal charges e of the same sign in air ($\epsilon = 1$) is given by $f = e^2/r^2$. If the charges are equal but unlike in sign, as in Figure XC, the force is $f = (+e)(-e)/r^2$, so that

$$f = -\frac{e^2}{r^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(i)}$$

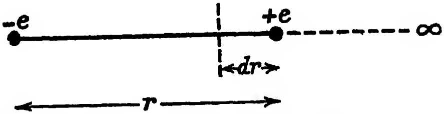


FIGURE XC—INTERACTION OF TWO OPPOSITE CHARGES

Thus attractive forces are reckoned negatively (repulsive forces positively). The potential energy J in the attractive case under consideration is measured by the work W done *by* the force in bringing either charge in the figure from an infinite distance to within distance r of the other, but with *sign reversed*. Suppose, therefore, that one of the charges is moved through an infinitesimal distance dr by the force f; the work done is $f\,dr$, so that

$$-J = W = \int_\infty^r f.dr = \int_\infty^r -\frac{e^2}{r^2}\,dr = -\int_\infty^r \frac{e^2}{r^2}\,dr$$

$$= -\left\{\left[-\frac{e^2}{r}\right]_{r=r} - \left[-\frac{e^2}{r}\right]_{r=\infty}\right\} = +\frac{e^2}{r},$$

whence

$$J = -\frac{e^2}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(ii)}$$

The field at distance r from charge $+e$ is given by putting $e_1 = 1$ in the expression $f = e.e_1/r^2$, since the intensity of field is measured by the force on *unit* charge. This gives for the field

$$F = \frac{e}{r^2} \quad \cdots\cdots\cdots\cdots \quad \text{(iii)}$$

The potential of the field, or work done on unit charge in bringing it from infinity to distance r is then given by a similar integration to the above as e/r.

(2) **Ion and Dipole** (Figure XCI).

(a) *Rigid Dipole* Let a dipole of moment m and dipole length $2s$ be considered in relation to a charge $+e$ placed along the axis

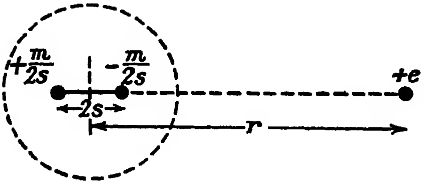


FIGURE XCI.—INTERACTION OF ION AND DIPOLE The case considered is that of the centre of the ionic charge lying on the line of the dipole axis.

of the dipole produced at a distance from its centre r, as in Figure XCI, with the negative end of the dipole lying towards the positive ion, so that the force of attraction predominates. The pole strengths are given by $+m/2s$, $-m/2s$. Then it follows that the net force f is given by

$$f = \frac{me}{2s}\left[\frac{1}{(r+s)^2} - \frac{1}{(r-s)^2}\right] = \frac{me}{2s}\left[\frac{-4rs}{r^4 - s^2(2r^2 - s^2)}\right]$$

If, now, s is very small compared with r, neglecting the second term in the denominator,

$$f = -\frac{2me}{r^3} \quad \cdots\cdots\cdots\cdots \quad \text{(iv)}$$

whence the potential energy J of the rigid dipole in the field F is given by

$$-J = W = \int_{\infty}^{r} -\frac{2me}{r^3}\,dr = \left\{\left[\frac{em}{r^2}\right]_{r=r} - \left[\frac{em}{r^2}\right]_{r=\infty}\right\} = +\frac{me}{r^2}$$

whence, using (iii) above,

$$J = -mF \quad \cdots\cdots\cdots\cdots \quad \text{(v)}$$

where m must be replaced by $m\cos\theta$, if the dipole axis lies at an angle θ with the direction of the field.

In accordance with (iv), the force between a dipole and a charged ion varies inversely as the *cube* of the distance separating centres.

(b) *Induced Dipole.* Imagine now that the dipole in Figure XCI was originally induced by the charge e. In this case, the potential energy will be different, since energy is used in deformation whereby the dipole arises. Let a be the polarizability of the atom or molecule in which the dipole is induced. Then it is assumed that $m = aF$ (see equation (4) of Chapter XI), so that m is given, using (iii), by

$$m = \frac{ae}{r^2} \qquad \text{(vi)}$$

Application of the Coulomb Law will then lead to equation (iv) as in the case of the rigid dipole, so that, combining (iv) and (vi), the " quasi-elastic " force f_1 is given by

$$f_1 = -\frac{2ae^2}{r^5} \qquad \text{(vii)}$$

so that f_1 varies inversely as the *fifth* power of the distance between centres. The corresponding potential energy J_1 is found by integration:

$$-J_1 = W_1 = \int_\infty^r -\frac{2ae^2}{r^5}\,dr = \left(\left[\frac{ae^2}{2r^4}\right]_{r=r} - \left[\frac{ae^2}{2r^4}\right]_{r=\infty}\right). \\ = \frac{ae^2}{2r^4} = \frac{me}{2r^2},$$

so that

$$J_1 = -\frac{1}{2}mF \qquad \text{(viii)}$$

The net potential energy J_2 in the case of the induced dipole is the difference between the energy of the rigid dipole and the energy necessary to set it up, whereby $J_2 = J - J_1$, so that, by (v) and (viii), J_2 is numerically equal to J_1 as given by the last equation Since $m = aF$, and $e = Fr^2$, J_2 may be expressed in the following ways:

$$J_2 = -mF/2 = -m^2/2a = -aF^2/2 = -em/2r^2$$

(3) **Two Dipoles in Line** (Figure XCII).

Let two dipoles lie end-on, as in Figure XCII; required the potential energy of the system, in terms of the distance between centres r and the moment m. The case considered is that of two exactly like dipoles. The force acting is given by a Coulomb summation·

$$f = \frac{m^2}{s^2}\left[\frac{2}{r^2} - \frac{1}{(r+s)^2} - \frac{1}{(r-s)^2}\right] = \frac{m^2}{s^2}\left[\frac{-6r^2s^2 + 2s^2}{r^6 - r^2s^2(2r^2 - s^2)}\right],$$

which leads, neglecting the second terms in numerator and denominator, to the following expression:

$$f = -\frac{6m^2}{r^4} \quad \ldots\ldots\ldots\ldots \quad \text{(ix)}$$

This gives the law of force between two dipoles as varying as the inverse *fourth* power of the distance separating their centres. The corresponding potential energy is given by integration as in previous cases by the relation

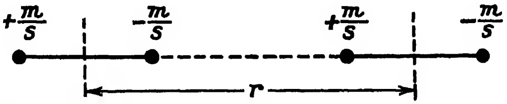


FIGURE XCII—INTERACTION OF TWO DIPOLES. Case I. Dipole axes lying along the line of centres.

$$J = -\frac{2m^2}{r^3} \quad \ldots\ldots\ldots\ldots \quad \text{(x)}$$

When the dipoles are unlike, of moments m_1, m_2 the corresponding expression is found to be $-2m_1m_2/r^3$. In the still more general case where the dipoles are unequal and arranged at angles θ_1, θ_2 to the direction of the line joining their centres, the expression is in the attractive case (Figure XCIII)·

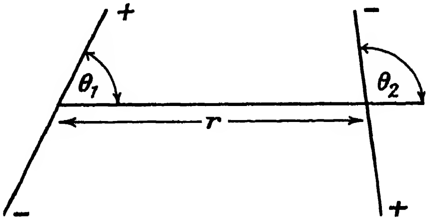


FIGURE XCIII—INTERACTION OF TWO DIPOLES Case II Dipole axes inclined to the line of centres at angles θ_1, θ_2

$$J = -\frac{m_1m_2}{r^3}(\sin\theta_1\sin\theta_2 - 2\cos\theta_1\cos\theta_2).$$

The case $\theta_1 = 0°$, $\theta_2 = 180°$ then leads to the end-on position of Figure XCII, putting $m = m_1 = m_2$, equation (x) is obtained.

Further calculation on the same lines shows that more symmetrical arrangements of charges as in quadrupoles and octupoles give laws of force which vary as higher powers of the distance r.

(4) **The Water Molecule** (Figure LXXXVI).

Let the triangular model of the water molecule shown in Figure LXXXVI represent the structure, with the oxygen atom carrying charge $-2e$ at the point O, and with the two hydrogen atoms H at distance r from O, each atom carrying charge $+e$ at distance s apart. Then the dipole axis lies along OK, with the negative end towards the two hydrogen atoms. Let a moment be regarded as positive if it points in direction from O to K.

The *natural dipole* of the model corresponds to a charge $-2e$ at O and $+2e$ at K. The moment is $2e.\text{OK} = 2er\cos\theta$. The *induced dipole* (in the opposite direction) is given by $-aF = -a\frac{2e}{r^2} . \cos\theta$, since the field is e/r^2 along each limb of the model. The total moment μ is then given by

$$\mu = 2er\cos\theta - \frac{2ea}{r^2}\cos\theta \quad .. \quad ... \qquad \text{(xi)}$$

The procedure is next to evaluate the potential energy J, and use the condition for stability that this shall have a minimum value. J is given by

$$J = -\frac{2e^2}{r} - \frac{2e^2}{r} + \frac{e^2}{s} - \frac{aF^2}{2}$$

using one of the expressions for the potential energy of an induced dipole as derived under (viii) (p 450). From this, since $s = 2r\sin\theta$ and $F = 2e\cos\theta/r^2$, it follows that

$$J = -\frac{e^2}{r}\left[4 - \frac{1}{2\sin\theta} + \frac{2a}{r^3}\cos^2\theta\right],$$

whence, by differentiation,

$$\frac{dJ}{d\theta} = -\frac{e^2}{2r}\cos\theta\left[\frac{1}{\sin^2\theta} - \frac{8a}{r^3}\sin\theta\right].$$

The condition for minimum potential energy is $\frac{dJ}{d\theta} = 0$, so that

EITHER $\cos\theta = 0$ (corresponding to a linear symmetrical model previously ruled out), OR

$$\sin^3\theta = \frac{r^3}{8a} \quad \ldots\ldots\ldots\ldots \tag{xii}$$

This condition evidently corresponds to a triangular model having permanent moment Since $\sin\theta$ must lie between the limits 0 and 1, the condition $\frac{a}{r^3} > \frac{1}{8}$ must be satisfied.

The next step involves the introduction of the moments of inertia of the molecule about the X and Y axes, written I_x and I_y At O, there is a mass $w_2 = 16a$ due to the oxygen atom, and at the ends of the limbs masses $w_1 = a$ due to the hydrogen atoms, where a is the unit of mass, so that the mass of the water molecule on this scale $= w_2 + 2w_1 = 18a$. By the condition of moments, $w_2 l = 2w_1 n$, where $OC = l$, $CK = n$, giving $n = 8l$ (Figure LXXXVI). This yields $l = \frac{1}{9}(l+n) = \frac{1}{9}r.\cos\theta$, and $n = \frac{8}{9}(l+n) = \frac{8}{9}r.\cos\theta$. The moment about the X axis is then $I_x = w_2 l^2 + 2w_1 n^2 = 2a(8l^2 + n^2)$ by the definition of moment of inertia, whence, substituting the above values of l and n, it follows that

$$I_x = \frac{16a}{9} r^2 \cos^2\theta \quad \ldots\ldots \tag{xiii}$$

Further, I_y is equal to $2w_1(s/2)^2$, so that

$$I_y = 2ar^2\sin^2\theta \quad \ldots\ldots\ldots \tag{xiv}$$

Dividing (xiv) by (xiii), it is found that

$$\tan^2\theta = \frac{8}{9} \cdot \frac{I_y}{I_x} \quad \ldots\ldots \tag{xv}$$

Eucken (ref. [304] of Chapter XIII) gave the following values of the three moments of inertia of the water molecule $I_1 = 2{\cdot}25 \times 10^{-40}$, $I_2 = 0{\cdot}98 \times 10^{-40}$, $I_3 = I_1 + I_2 = 3{\cdot}2 \times 10^{-40}$, where I_3 corresponds to rotation about the centre C in the plane of the paper Uncertainty then exists as to whether (a) $I_x = I_1$ and $I_y = I_2$, or (b) $I_x = I_2$ and $I_y = I_1$ Substitution of Eucken's values gives (a) $\theta = 32°$, (b) $\theta = 55°$. Debye favoured the former alternative by the following argument.

Eliminating a between (xi) and (xii),

$$\mu = 2er\cos\theta\left[1 - \frac{1}{8\sin^3\theta}\right]$$

whence for (a) $\theta = 32°$,

$$\frac{\mu}{2er} = 0{\cdot}131 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(xvia)}$$

and for (b) $\theta = 55°$,

$$\frac{\mu}{2er} = 0{\cdot}443 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(xvib)}$$

Now from (xiii) and (xiv), using $\sin^2\theta + \cos^2\theta = 1$,

$$r^2 = \frac{8I_y + 9I_x}{16a},$$

whence substituting a = mass of hydrogen atom $= 1{\cdot}66 \times 10^{-24}$ gram, for case (a)

$$r = 1{\cdot}07 \times 10^{-8} \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(xviia)}$$

and for case (b)

$$r = 1{\cdot}02 \times 10^{-8} \quad \ldots\ldots\ldots\ldots \quad \text{(xviib)}$$

These values of r are now substituted in (xvia) and (xvib) respectively, giving

$$\mu = 1{\cdot}34 \times 10^{-18} \quad \ldots \quad \text{(xviiia)}$$

and

$$\mu = 4{\cdot}32 \times 10^{-18} \quad \ldots \quad \text{(xviiib)}$$

The former value corresponds more closely to experiment (Jona found $1{\cdot}87 \times 10^{-18}$). The values of a may now be obtained from equation (xii) and hence the polarization P can be calculated by means of the relation $P = \frac{4\pi}{3} Na$. The two possible models then give the following values ·

	θ	r	a/a^3	P	μ
Case (a)	32°	$1\ 07 \times 10^{-8}$	0·848	2·64	$1{\cdot}34 \times 10^{-18}$
Case (b)	55°	$1\ 02 \times 10^{-8}$	0·227	0·617	$4\ 32 \times 10^{-18}$

Wasastjerna gave $P_{0}-- = 4{\cdot}06$, hence it is concluded that the hydrogen atoms enter the outer shell of the oxygen atom Similar models are probable for hydrogen sulphide, sulphur dioxide and ethyl ether.

(5) **The Ammonia Molecule** (Figure XCIV).

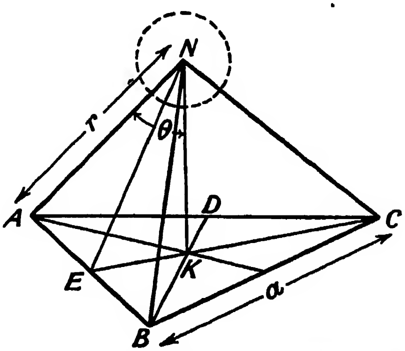


FIGURE XCIV—STRUCTURE OF THE AMMONIA MOLECULE.

A calculation similar to that carried out above leads to the following expression for the moment of the ammonia molecule:

$$\mu = -\frac{9e^2}{r}\left[1-\frac{1}{3\sqrt{3}\sin\theta}+\frac{a}{2r^3}\cos^2\theta\right] \ldots\ldots\ldots \quad \text{(xixa)}$$

This leads to the alternatives: $\cos\theta = 0$, yielding a plane model without moment, therefore rejected; and

$$\sin^3\theta = \frac{1}{3\sqrt{3}}\cdot\frac{r^3}{a} \quad \ldots \quad . \quad \text{(xixb)}$$

which corresponds to a pyramidal structure shown in Figure XCIV. The hydrogen atoms are at A, B and C.

(6) **Two Equal Dipoles Set at an Angle ϕ** (Figure LXXXVI).

Let us consider two moments $\mu' = 1$ acting at an angle $\phi = 2\theta$, the resultant acting along OK (Figure LXXXVI). Then, neglecting induction, the resultant is $2\mu'\cos\theta = 2\mu'\cos\phi/2 = 2\mu'\sqrt{(1+\cos\phi)/2}$, whence

$$\mu = \mu'\sqrt{2(1+\cos\phi)} \quad \ldots\ldots \quad \ldots\ldots \quad \text{(xx)}$$

(7) Three Equal Dipoles Set at an Angle θ (Figure XCIV).

Let three dipoles of moment $\mu' = r$ act along NA, NB, NC in Figure XCIV, mutually inclined to each other at an angle θ, and let the sides of the triangle ABC be represented vectorially by moments equal to a. We have

$$BK = \frac{2}{3}BD = \frac{2}{3}\sqrt{BA^2-AD^2} = \frac{2}{3}\sqrt{{}^2-a\frac{a^2}{4}} = \frac{2}{3}\sqrt{\frac{3a^2}{4}} = \frac{a}{\sqrt{3}}$$

Further, $NK = \sqrt{BN^2-BK^2}$, so that the resultant moment along NK is

$$\mu = 3\sqrt{\mu'^2-\frac{a^2}{3}} \quad \ldots\ \ldots\ldots\ldots\ldots \quad \text{(xxi)}$$

Now

$$\sin\frac{\theta}{2} = \frac{AE}{AN} = \frac{a}{2\mu'},$$

so that

$$\frac{a^2}{4\mu'^2} = \sin^2\frac{\theta}{2} = \frac{1-\cos\theta}{2},$$

whence

$$a^2 = 2\mu'^2(1-\cos\theta) \quad \ldots \quad \ldots\ldots \quad \text{(xxii)}$$

Substituting this value of a^2 in (xxi),

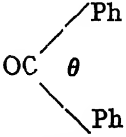
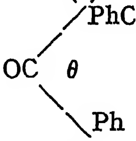
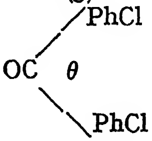
$$\mu = 3\mu'\sqrt{\frac{3-2(1-\cos\theta)}{3}} = 3\mu'\sqrt{\frac{1+2\cos\theta}{3}}$$

whence

$$\mu = \mu'\sqrt{3(1+2\cos\theta)} \quad \ldots\ \ldots\ \ldots\ \ldots \quad \text{(xxiii)}$$

Induction is neglected in the above argument.

(8) Example of Calculation of Moment (see Bergmann and Engel, ref. 189 of Chapter XIII).

	(1)	(2)	(3)	(4)
				PhCl
	Benzophenone	*p*-chloro-benzophenone	*p*. *p*'-dichloro-benzophenone	chlorobenzene
μ (Expt.) $\times 10^{18}$	2·95	2·70	1·64	1·56

Let us calculate the moment of (2) $= \mu_2$, assuming moments of (1), (3) and (4) $= \mu_1, \mu_3, \mu_4$ respectively.

Considering the molecule (2), we have

$$\mu_2 = \sqrt{\mu_1{}^2 + \mu_4{}^2 + 2\mu_1\mu_4\cos\frac{\theta}{2}} \quad \cdots \quad \cdots \tag{xxiv}$$

Assuming $\mu_{\text{Ph}} = 0$, and angle θ is constant,

$$\mu_3 = 2\mu_4\cos\frac{\theta}{2} + \mu_1 \quad \cdots\cdots \quad \cdots\cdots \tag{xxv}$$

Whence, combining (xxiv) and (xxv),

$$\mu_2 = \sqrt{\mu_4{}^2 + \mu_1\mu_3} \quad \cdots \quad \cdots \quad \cdots \quad \cdots\cdots \tag{xxvi}$$

Inserting $\mu_4 = 1{\cdot}56$, $\mu_1 = 2{\cdot}95$, $\mu_3 = 1{\cdot}64$, (xxvi) gives $\mu_2{}^2 = 7{\cdot}27$, as against experimental value $\mu_2{}^2 = 2{\cdot}70^2 = 7{\cdot}29$.

LIST OF AUTHORS CITED IN REFERE

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Notes —Roman numerals refer to reference lists, other numbers to references in lists. The symbol H denotes Head of list, where a book is cited. " App " refers to the reference list to the Appendix to Part I on page 214. In cases where two or more authors have the same name and initials, separate classification is not adopted Where the same author gives different initials in different papers, he may appear more than once in this list A complete list of names in the subjects treated in this volume is obtained by combining the list below with the names in the three works mentioned in the Preface to Volume II (page xxi).

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